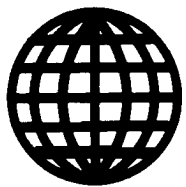


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JAPAN

11TH AIST TSUKUBA GENERAL SYMPOSIUM

926C0071 Tokyo SEKAI NI HABATAKU JISEDAL PUROJEKUTO in Japanese 19 Feb 92
pp 1-167

[Papers presented at the 11th AIST Tsukuba General Symposium: 10th Anniversary of the R&D Project of Basic Technologies for Future Industries "Jisedai Project" held 19-20 Feb 1992 in Tsukuba City, sponsored by the AIST, MITI]

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High Tech, International Contribution

926C0071A Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 3-6

[Text] 1. Japan and United States Lost Their Purpose

United States: Breakup of USSR

Japan: Caught up with Europe and United States

2. International Outlook on Advanced Technology

Scenario 1: Pessimistic

Japan's manufacturing industry strengthens global dominance
United States fortifies technical nationalism after losing past
glory
EC strengthens regional ties

Scenario 2: Optimistic

United States absorbs Japanese production technologies
Japan makes global contribution in basic research
EC cooperates with United States and Japan

Scenario 3: Intermediate

Provided that policies to handle the following are established:

- (1) Deepening gap between the triangle and other regions
- (2) Worsening of earth's environment

3. Global Contributions Are Vital From Technoglobalism Standpoint

May have to assume technical instruction stance. Some positive measures are described below.

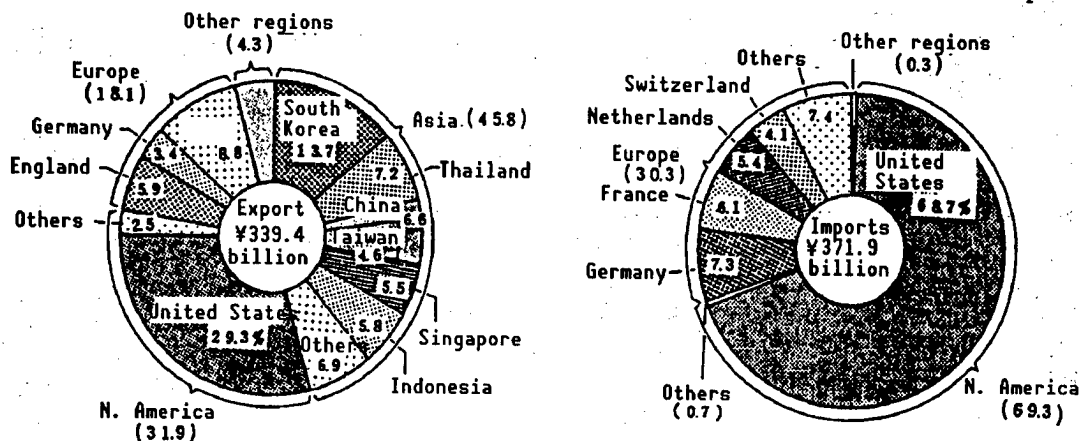
4. Technology Transfer

4.1 Technology Trade for Different Countries

Japan → Asia to Japan → United States, Europe

United States → Japan, fixed

Europe → Japan must also be expanded



Source: "Overview of Survey Results on Science & Technology for 1991" by Statistics Department, Administrative Department

Figure 1. Composition (by Country) of Technology Exchange (Technology trade) (FY 1990)

4.2 Change in Type of Technology Transfer

From mature industries to high technology

Industry	Technology export		Technology import	
	FY 1985	FY 1990	FY 1985	FY 1990
	Amount received (¥ billion)	Amount paid (¥ billion)	Amount received (¥ billion)	Amount paid (¥ billion)
Whole industry	2,342	3,394	2,932	3,719
Manufacturing	2,056	3,207	2,886	3,683
Fiber	40	39	33	47
Chemical	382	582	374	540
Iron and steel	262	94	47	65
Telecommunications, electronics, electrical measuring instruments	417	677	601	1,224
Automobile	260	889	114	76

Source: "Overview of Survey Results on Science and Technology in 1991" by Statistics Department, Administrative Department

4.3 Borderless Technology

5. Joint Technological and R&D Efforts

5.1 Joint Efforts With Technologically Advanced Nations

IMS

FSX, passenger planes, engines

Atomic energy (nuclear fusion), space (station, satellite launching vehicle)

5.2 Joint Efforts With Developing Nations

Strengthen joint technological efforts as part of ODA program

Introduction of advanced technology to mature industries as part of joint research efforts

Agricultural and fisheries industry, medical equipment, educational materials (information database)

6. Environmental Problems

Measures against destruction of ozone layer, earth "warming"

Stop usage of fossilized fuel (use of atomic energy, solar energy)

Energy conservation technologies

7. Contributions Through Basic Research

1980 respected technologies (from #2 to #1)

Technologies that are a threat

1990 start of basic research

Japan too must trace the road the United States has traveled since 1990.

Basic research

Human Frontier Science Program to understand life, living animals, and humans

To understand about earth and space

To understand about matter (e.g., principles of superconducting)

What is a field?

Generic technology

1981 Jisedai Project (R&D Project of Basic Technologies for Future Industries)

ERATO Project (Exploratory Research for Advanced Technology Operation Project)

10-Year Old Path for Next-Generation Project

926C0071B Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 7-8

[Text] 1. Introduction

What is the Next-Generation Project?

- (1) Transition from development of applied technology to basic technology.....New materials, biotechnology, new function elements
- (2) Global contributions in technology as befitting a major economic nation.....Criticism of stolen basic research

What is the R&D target?....From "bud" to "young tree."
Revolutionary, trendy, advanced basic research

Powerful liaison between industry, academia, and government

.....Requisition of a coordinator, Initiative by researchers.

Flexible R&D system

.....Parallel developments. Mid-term evaluations.

2. Background Behind Establishment of Next-Generation Project

Towards a technology-based nation.....Vision key word in 1980s.

Establishment of "Next-Generation Project" in August of 1980

.....The key to a technology-based nation

Project kicked off with basic technologies in 12 themes in three fields
(Phase One)

(1) New material

Plain and inconspicuous existence → vital for advancing and intensifying knowledge on industrial structure

(2) Biotechnology

Gene rearrangement → revolutionize chemical industry, solutions to energy and environmental problems

(3) New function element

Arrival of highly advanced information society 20 years later → limit of age of very large-scale integration (VLSI)

3. New Developments in Next-Generation Project

(1) Upgrade to global results and reality phase

(2) Studies for new developments

"46 pioneer basic technologies in 21st century"

(3) Development of "Phase Two"

Employment of more advanced new research themes with shifted basics
Diversification of R&D.... "superconductivity," "software"
Use of intensive research method
Strengthen global joint efforts

(4) Increased promotion of technology development by private corporations

By New Energy Development Organization (NEDO)
Revision of industrial rights ownership.... private 50%, global joint research 100%

4. Future Issues

Technoglobalism.....Vision key word for 1990s

Science and technology becomes global hot issue....."SSC," intelligent property ownership

**Trends in Science and Technology Policies in United States and Japan

Future significance of technology development projects.....Improvement of technology development powers by private sector?

Future of Next-Generation Project.....Future significance in industrial basic technologies

R&D Trends, Future Issues in Superconducting Materials

926C0071C Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 11-38

[Article by Shoji Tanaka, professor, Tokai University, professor emeritus, University of Tokyo, deputy director, International Superconducting Industrial Technology Center (ISTEC)]

[Text] 1. Introduction

High-temperature superconducting materials were discovered five years ago. Although the critical temperature increase has leveled off, significant advances were made in the characteristics and applications of existing materials. R&D has entered Phase Two. A strong magnetic floating effect resulting from a significant increase in the critical electric current was recently observed. Potential applications are being continuously developed and by the mid 1990s, a market may even appear.

The development history based on results in the past three years from the International Superconducting Industrial Technology Research Center and future issues will be briefly described.

2. Search for New Matter

The search for new superconducting matter was mainly targeted at the 1) clarification of superconducting mechanism, and 2) development of materials with higher T_c .

New superconducting materials may be developed by transforming existing matter into superconductors, raising T_c of existing materials or searching for a completely new material.

2.1 Transformation of Existing Matter Into Superconductors

The configuration shown in Figure 1 is commonly referred to as infinite lamina. Its chemical formula is given by $ACuO_2$. To date, $(Sr,Ca)CuO_2$ is synthesized, does not display superconductivity properties and is nonmagnetic with $T_N = 537 \pm 5$ K.¹ Smith, et al.,² has synthesized $Sr_{1-x}Nd_xCuO_2$ ($0.14 \leq x \leq 0.16$) at 1,000°C and 25,000 atmp with $T_c = 40$ K. Takano, et al.,³ treated

$(\text{Sr,Ca})_{0.9}\text{CuO}_2$ with the oxidizing agent, KClO_3 at $1,000^\circ\text{C}$ and $60,000$ atmp and proved superconductivity of $T_c = 110$ K.

The new configuration shown in Figure 2 was discovered by Roth, et al.,⁴ Cava, et al.,⁵ observed Meisner signals of $T_c = 35$ K from $\text{GaSr}_2(\text{Er}_{0.6}\text{Ca}_{0.4})\text{CuO}_y$ after being treated in an oxygen environment for 48 hours at 950°C and 25 atmospheres. SRL has proved that $(\text{Ga,Cu})\text{Sr}_2(\text{Y,Ca})\text{Cu}_2\text{O}_y$ displayed $T_c = 50$ K.⁶

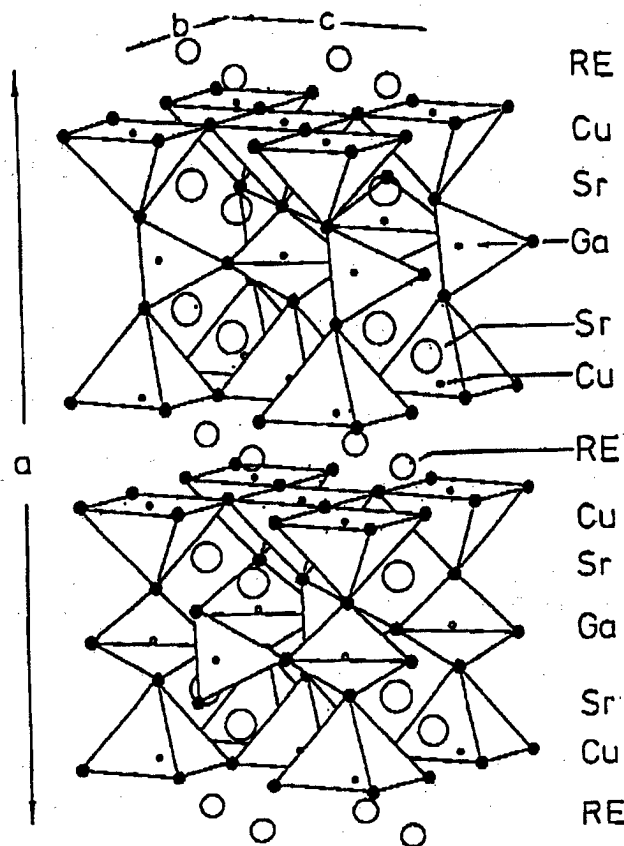


Figure 2. Crystal Structure of $\text{GaSr}_2\text{RECu}_2\text{O}_7$ (KFK Roth, et al.)

ly synthesized new Cu butoxide. $T_c = 90$ K bulk was synthesized by the sol-gel process. This is a flat crystal and is useful for material processing.

2.2 Increasing T_c

The maximum T_c value to date is that for TI-2223 phase at 125 K. SRL has, by the process shown in Figure 3, succeeded synthesizing TI-2223 phase that displayed $T_{CR} = 0 - 127$ K, $T_{cmag} = 130$ K (Figure 4).¹⁰ This was further confirmed at Cambridge University and also conforms with recent IBM data.

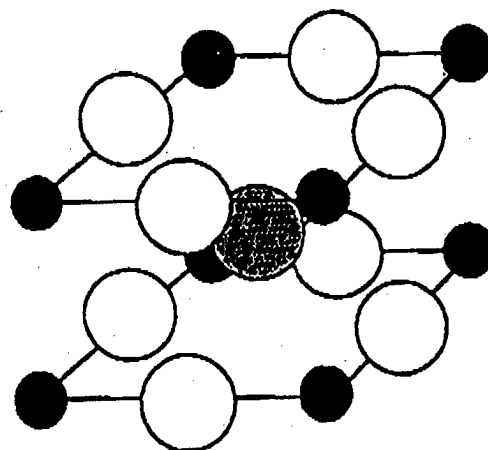


Figure 1. Infinite Layer-Crystal Structure

(•: Cu; o: Oxygen;
center: Alkali earth metal)

(Pb,Cu) -1222 phase possesses the fluorspar configuration. SRL first succeeded in fabricating this superconducting phase in 1990.⁷ It was discovered that treatment of $(\text{Pb,Ca})(\text{Sr,Ln})_2(\text{Ln,Ce})_2\text{Cu}_2\text{O}_y$ ($\text{Ln} = \text{Sm, Eu}$) under high pressure in an oxygen environment displays $T_c = 32$ K.⁸ Recently, Cava, et al.,⁹ was successful in synthesizing Nb-1222 under high pressure and an extremely narrow temperature range to produce superconductors of $T_c = 28$ K.

The 124 phase is normally synthesized under high pressure. In particular, synthesis of 90 K class Ca and doped 124 phase was said to be impossible under normal pressure and low temperature but this was proven wrong by SRL who successful-

Kaneko et.al. (1991)

Raw Materials
 Tl_2O_3 , BaO_2 , CaO , CuO
 Nominal Composition
 $Tl:Ba:Ca:Cu = 1.7:2.0:2.3:3.0$



Sintering
 at $890^\circ C$ for 5 hours in
 flowing O_2 gas



Encapsulation in evacuated
 fused quartz tube



Post Annealing
 at $750^\circ C$ for 250 hours

Zero Resistance : $126.9 K$
 Temperature
 Onset Temperature : $130.0 K$
 of Meissner Signal
 Nearly "2223" Single Phase

Parkin et.al.(1988)

Raw Materials
 Tl_2O_3 , BaO , CaO , CuO
 Nominal Composition
 $Tl:Ba:Ca:Cu = 1.0:1.0:3.0:3.0$



Encapsulation in fused quartz
 tube (in 1 atm O_2 gas)



Sintering
 at $880^\circ C$ for 3 hours

Zero Resistance : $125 K$
 Temperature
 Onset Temperature : $125 K$
 of Meissner Signal
 Mixed (Multiple) Phases

Adachi et.al.(1990)

Raw Materials
 Tl_2O_3 , $BaCuO_2$, Ca_2CuO_3 , CuO
 Nominal Composition
 $Tl:Ba:Ca:Cu = 1.0:1.0:3.0:3.0$



Encapsulation in evacuated
 fused quartz tube



Sintering
 at $760^\circ C$ for 720 hours

Zero Resistance : $124.9 K$
 Temperature
 Onset Temperature : $127.2 K$
 of Meissner Signal
 Mixed (Multiple) Phases

Figure 3. Comparison of Sample Preparation Methods and Properties ($I_c = 130 K$, $11-2223$ (Kaneko, et al.))

2.3 Other New Materials

A_xC_{60} was reported as superconducting in 1991. Maximum T_c was the 33 K¹¹ for Cs_2RbC_{60} . It is strongly possible for this to be explained within the limits of BCS theory.

3. Various Aspects of Matter

Clarification of physics of high-temperature superconductivity is extremely important in the search for new materials as well as the development of high-performance materials. Research has been actively pursued. High-temperature superconductors do not only possess the superconducting state but various "abnormal" phenomena have been reported at the normal conducting state. A temperature dependent change in resistivity over a wide-temperature range, a Hall constant that changes significantly at low temperature, a large increase in nuclear magnetic resonance (NMR) at values exceeding T_C , and an electron excited Raman dispersion up to high energy levels are some examples. No theory can explain such behavior without contradiction but, the properties of superconducting oxides are now very much clearer.

Firstly, high-temperature superconductivity occurs when an appropriate amount of conducting carriers are introduced in the laminated copper oxide insulating substrate made of $Cu-O_2$ surfaces. La_2CuO_4 or $YBa_2Cu_3O_6$ are some insulator substrates. The substrates display normal metallic conducting properties when doped with more carriers. In the superconducting layer, electron correlation is believed to be quite strong. From research on photon matter of photoelectron spectroscopy, carrier introduction creates a type of intragap condition where charges transition from 2p level in oxygen to the upper 3d in Cu. The electron condition density was found to be very high at the Fermi plane. High-temperature superconductors, like metals, have pairs of Fermi particles bonded together by some form of attractive power. Bose contraction is a correct description. Much work has been performed on the gap resulting from pair formation by infrared, Raman, tunnel, and photoelectron spectroscopy. As was discovered from the BCS theory, it is forecast that the gap ranges from 3.5 kT_c to 8-10 kT_c .

Anisotropy in the kinetic direction of the gap was previously believed nonexistent but recent photoelectron spectroscopic experiments have made opinions swing in the other direction.

High-temperature superconducting phase occurs when the long-range order of the strongly antimagnetic Cu spin resulting from carrier introduction, tires. As a result, the correlation relationship between magnetism and superconductivity is most interesting and many studies on neutron dispersion, NMR, and Raman dispersion are in progress. The hole carrier in La or Y are known to enter 2p

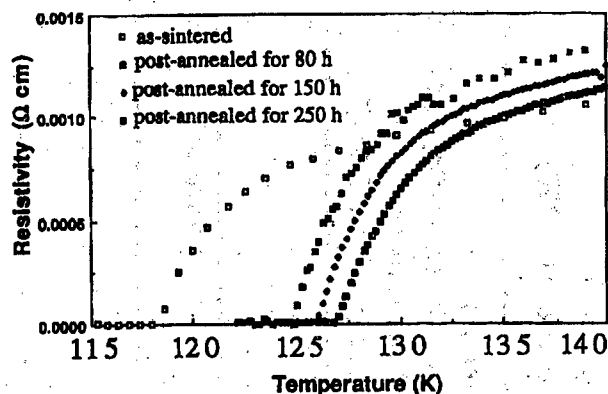


Figure 4. Relationship Between Resistivity-Temperature for Tl-2223 Phase (Kaneko, et al.) ($Tl_{1.7}Ba_2Ca_{2.3}Cu_3O_2$)

orbits of O and form strong nonparallel spin bonds with the Cu 3d spin. As a result of hole introduction, the neighboring inter-Cu spin bonds are rendered unstable and the unstable spin reduces the strong magnetic correlation. The main problem is how much correlation remains when the substance is in the superconducting state. Correlation that depends on neutron dispersion and/or NMR has been reported in the sample when in the superconducting state although these do not necessarily match. Based on this, a theory was proposed for explaining the contribution of unstable spin to an increase in, for example, temperature dependency of resistance at temperatures above T_c or NMR.

One of the reasons for the delay in clarifying the physics concerning high-temperature superconductivity is because it is extremely difficult to obtain high quality single crystals with low structure irregularities and uniform configuration. Not only Bi base of Tl base as well as La214, Y123 is also similar. In this sense, Y124 is comparatively more stable than Y123 in terms of amount of oxygen. Since these are not replaced systems like La214, it is attracting a lot of attention as a base with few irregularities. We have measured the various physical properties for Y124 and compared them to Y123. The results are listed in Table 1. It is apparent from the resistivity or Hall constant that Y124 is more metallic and has more holes than Y123. The Ca replacement effects at T_c , pressure dependency, temperature dependency of NMR Nightshift (K) indicate that the number of holes are few and correlation between Cu spins are strong. The confirmation of this as simply due to a difference in the conductivity of CuO chain site will be a future issue.

Table 1. Comparison of Properties of Y124 and Y123 (SRL-ISTEC)

	Y123	Y124
T_c (K)	90	80
T_c (K) increase due to replacement	Nil	C_a replacement T_c rises to 90 K
T_c 's pressure dependence, dT_c/dP (K/GPa)	0.8	5.5
Resistivity ($\mu\Omega\text{cm}$, 100 K)	200	100
Hole constant R_H ($10^{-4}\text{cm}^3/^\circ\text{C}$, 300 K)	5	0.7
Specific heat difference ΔC (mJ/K ₂ mol)	47	15.5
Temperture dependence of oxygen NMR nightshift	Constant	Decrease when near T_c

Systems like Bi or Tl are strongly two-dimensional and the mechanism of their magnetic flux is particularly interesting. The magnetic flux quantum in a mixed state displays a phenomenon called magnetic flux creep of magnetic flux flow where the quantum is transported by the magnetic field, temperature, or the electric current. The clarification of phase shift when the magnetic field changes from a regular lattice to a fused state or the phenomenon of release from the pin stop, are very important issues in the development of materials that have high critical current density. The radius of the magnetic field quantum is about equal to the coherence length and this is approximately on the order of 20 Å or the size of an atom. Studies on detailed structure and

configuration of the surface and boundaries with the help of a transmission electron microscope (TEM) or a scanning tunnel microscope (STM) will become more important.

Various models based on electron lattice interaction, local distortions in the lattice, unstable electron charges, and unstable magnetism have been proposed to explain the symmetrical configuration mechanism but no specific explanation exists as yet. The various abnormal phenomena in normal conducting states are essential for explaining the symmetrical configuration.

4. Process Development

4.1 Directional Solidification Process

As part of the consideration on applications in line materials with high critical current density, studies were done on unidirectional solidification methods for improving the regularity of crystals in the 123 superconducting phase. The effects of the regularity of crystal fabricated by this unidirectional solidification method on the temperature gradient (G) and growth rate (R) are studied with the help of the horizontal Bridgmann directional solidification method. After fusing the temporarily burnt powder sample in a Pt crucible at 1,200-1,400°C, similar to the MPMG method, it is rapidly cooled and crushed. Then, it is fabricated into a stick-shape sample 5 mm in diameter and 10 cm long with the help of cold isostatic pressing (CIP). This sample is then placed inside a yttria stabilized zirconia tube crucible and unidirectionally solidified at a specific temperature gradient and drawn at a specific speed (growth rate). After sufficient solidification has progressed, the sample is drawn at a faster speed and rapidly cooled with the purpose of observing crystal/liquid phase boundary conditions during the solidification process. A smooth boundary was observed with a high G/R ratio (482 Kh/cm²) and unidirectional solidification was achieved. This is very similar to trends in principles underlying the theory of overcooled formation of alloys during solidification. Samples with high G/R ratio were observed from results of VSM magnetism curves (Figure 5) to have improved crystal regularity while Figure 6 shows that J_c values increase with G/R ratio. Cooling rate is given by GR and is a constant 6 K/h. The maximum J_c under these experimental conditions is 77 K and at 1 T, the critical current density observed is $1.9 \times 10^4 \text{ A/cm}^2$.

4.2 Hot Plasma Flush Vaporization Method

In the high-frequency hot plasma flush vaporization method, a powder is fed into ultrahot RF plasma to fabricate a powdered film by vaporization and condensation. This is an appropriate method for fabricating films with larger surface areas or at continuous high speeds. A superconducting film is obtained by feeding superconducting powdered oxide into hot plasma in an oxygen environment. Temporarily burnt powder with 123 configuration and average grain radius of about 3 μm was used as the powder raw material. Plasma fabrication was conducted under the following conditions: 4 MHz high frequency input: 50 kW; carrier gas: Ar 5 l/min; Sees gas: O₂ 50 l/min; pressure: 200 Torr. The sample reaches the specified temperature by altering the height of the supporting deck which is heated by the hot plasma. The temperature is

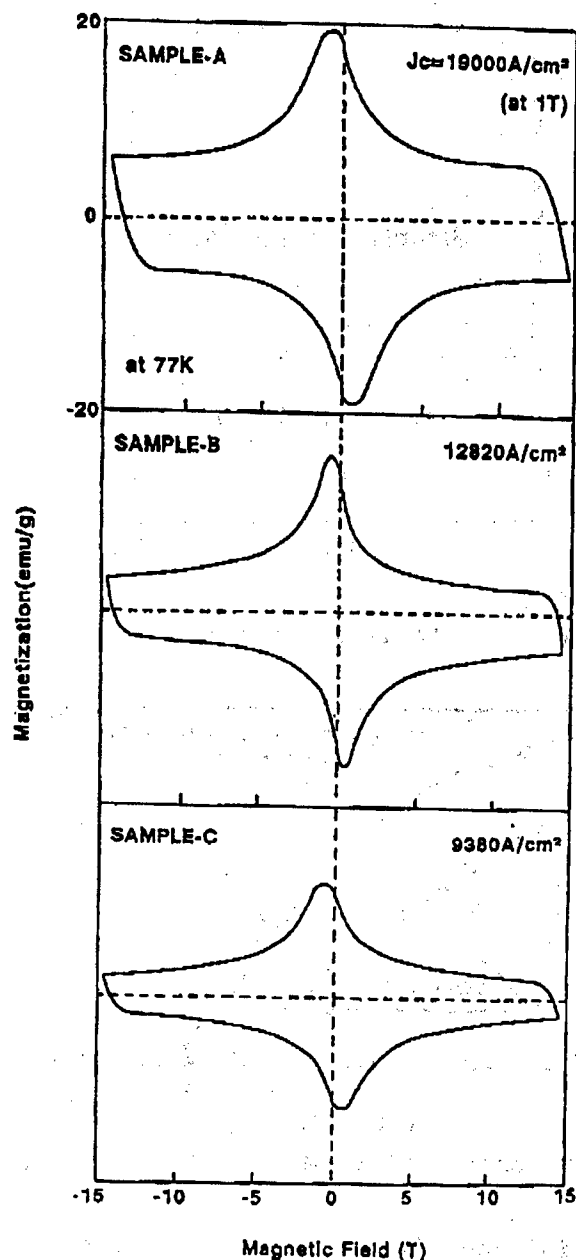


Figure 5. Magnetization Characteristics of Directional Solidifying Sample (123)

ture is the same, the crystal will adapt the c-axis configuration when the fabrication rate is slow and the a-axis when the rate is fast. For example, J_c characteristics of a film material with slow fabrication speed (A: 0.05 mm/min) and fast speed (B: 0.14 mm/min) whose holder temperature is 590°C were obtained by X-ray analysis. They are shown in Figures 7 and 8. T_c for A and B is 85.0 K and 80.1 K, respectively. As is apparent from the figures, sample A reached J_c values of 1.1×10^5 (A/cm²) at the liquid nitrogen temperature and

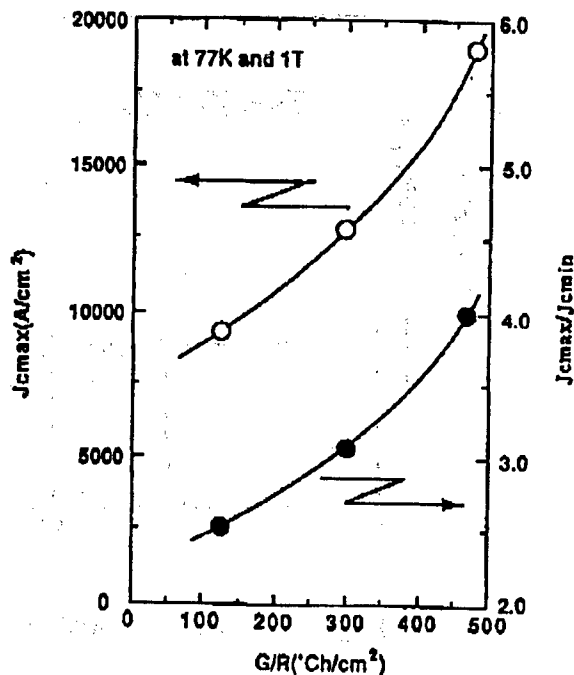


Figure 6. J_c -G/R Relationship for Directional Solidifying Sample (123)

monitored by a thermocouple fixed onto the supporting deck. The film fabrication rate was controlled by the quantity of the powder supply. The film was then naturally cooled in the 200 Torr environment. It was then removed from the chamber and its properties evaluated, after its temperature dropped to below 200°C in about 10 minutes. MgO-(100) was used for the substrate.

A superconducting phase was observed at a substrate (holder) temperature of above 500°C. Like other gaseous phase film fabrication methods, the crystal configuration changes from random or a-axis arrangement to one of c-axis arrangement when the temperature of the substrate increases. On the other hand, even when the fabricated film tempera-

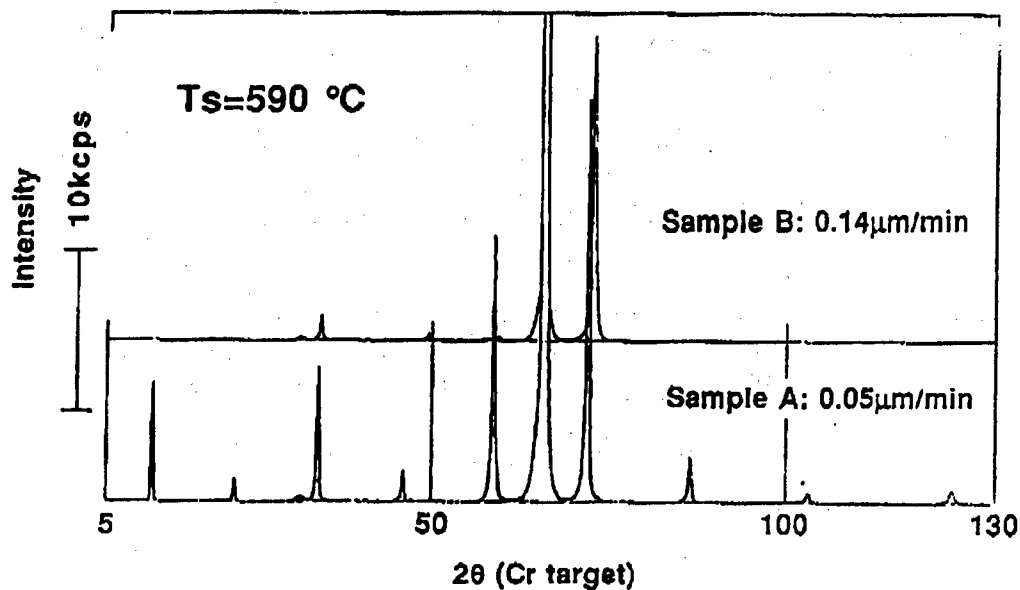


Figure 7. Film Growth Rate and X-Ray Analysis Pattern

$1.1 \times 10^6 (\text{A}/\text{cm}^2)$ at the liquid He temperature. This film fabrication speed is several hundred times faster than conventional phase growth methods. Promising methods to increase film fabrication speeds and higher quality thick films and tape materials can be produced by optimizing process parameters and altering types of substrates.

4.3 Process To Introduce Pin Check

Increase of the critical current density (J_c) is essential before superconducting materials can be commercialized. J_c increase can be achieved through the introduction of a nonuniform check to suppress flux movement in the superconductors. To date, various processes have been tested.

A typical example is the introduction of defects by irradiating the material with neutron beams, electron beams, gamma rays, or heavy ions. Significant increases in J_c by irradiation have been reported but it will be difficult to apply this method in commercially available materials.

A residual strata of insulating $\text{Y}_2\text{BaCuO}_5(211)$ remains within the configuration when Y-base material solidifies from its fused state. This indicates the superconducting layer ($\text{YBa}_2\text{Cu}_3\text{O}_{x:123}$) is generated by the crystal capping reaction. A material with many 211 phases is first identified as the

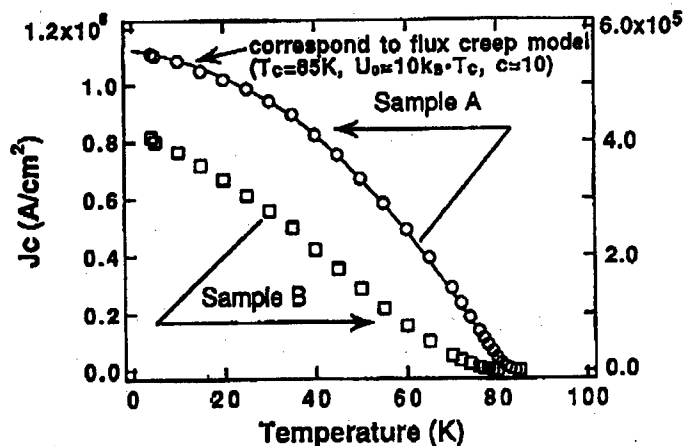


Figure 8. Effect of Film Growth Rate on J_c

originating material. It is then melted at high temperature, then crushed and powdered, the configuration controlled and finally cooled slowly to create a material with 211 phases dispersed within 123 phase. J_c measurements show that (in Figure 9) J_c values increase with the volume fraction of 211 phase and therefore acts as a form of check. Other examples include the intentional introduction of a nonsuperconducting phase in Bi, Tl base material besides Y-base material.

4.4 Platinum Doping Fusion Method

Y-base bulk superconductors have 211 phase finely distributed within the 123 crystal as microstructures and has high J_c values. This finely distributed particles of 211 phase acts as a crack check and is effective for oxygen dispersion. It is also promising as a pinning center. In the QMG or MPMG processes, microdispersion of 211 phase is achieved through the fused rapid cooling process or the fused growth process. We have recently discovered that doping with a slight quantity of platinum (<0.5 wt%) is effective in the microdispersion of 211 phase. In the platinum doping and melting method, the first step of melting and rapid cooling in the conventional process is replaced by platinum doping while the later melting and growth process is similar to the MPMG process. Crystal growing is done through slow cooling after partial melting at 1,100°C. J_c at 77 K and 1 T is about 20,000 A/cm² and is not a match for MPMG records, but, the important role played by platinum in the microdispersion of 211 phase also makes it an important tool for clarifying QMG and MPMG process mechanisms. Studies on doping effects of other elements in the same group as platinum showed that only rhodium has the same effects as platinum. Heated discussions are currently being held on the effects of platinum and no common views have been formulated yet, but it is believed that the formation of platinum, barium, and copper compound, $Ba_4CuPt_2O_9$ during the melting and growth process has some relation on the suppression of particle growth in the 211 phase.

5. From Thin Films to Devices

5.1 Laser Sputtering Method

5.1.1 Substrate bias effect

By applying a bias voltage of 300~500 V between the target and the substrate, superconductivity of the film can be improved. At the same time, oxygen plasma is generated between the target and the substrate.¹²

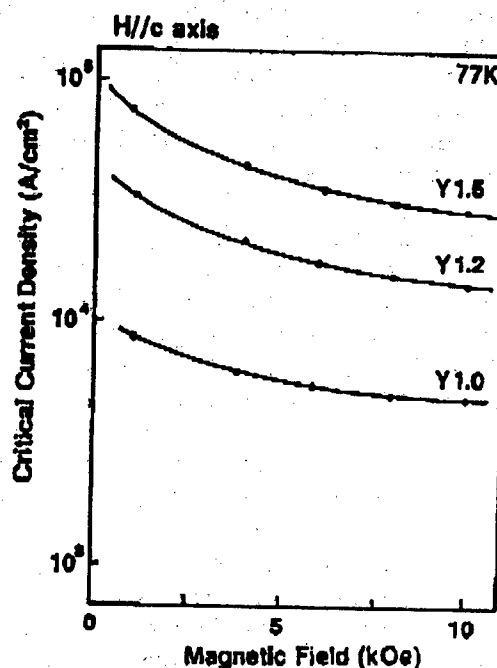


Figure 9. Dependence of J_c on Magnetic Field When Concentration of 211 Phase Is Increased (211 phase is Y1.0: 0%; Y1.2: 8%; Y1.5: 17%, respectively)

Multicharged ions of copper are also mixed¹³ in the scattered particles that make up the plume.

5.1.2 Oxygen pressure and crystal growth direction

When only the substrate temperature of a c-axis aligned film is lowered under its growth conditions, by about 100°C, the film transforms into an a-axis aligned film. The growth axis of the crystal will still change¹⁴ even when the substrate temperature is kept unchanged and oxygen pressure during sputtering is increased. The kinetic energy of the particles flying towards the substrate is low when aligned along the a-axis.¹⁵ As a consequence, on an appropriate substrate, epitaxy can be easily promoted when crystal growth is along the a-axis. In reality, a-axis aligned $\text{YBa}_2\text{Cu}_3\text{O}_7$ grown on NdGaO_3 displayed superior crystallinity.¹⁶

5.2 Microwave Devices

5.2.1 Laser sputtered film

Blisters of 10~100 nm on the surface of films fabricated by laser vapor deposition is unavoidable. In this sense, the off-axis vapor deposited film is better but the film growth speed is significantly slowed down. Ironically, films ($\text{YBa}_2\text{Cu}_3\text{O}_7$) with transition temperatures (T_c) exceeding 90 K has high surface resistance and therefore poor crystallinity. The T_c of films employed as materials in devices is around 85 K. This differs from bulk materials.

5.2.2 Resonators and band pass filters

A microstrip line resonator was fabricated using an MgO substrate with a laser vapor deposited film (350~400 nm) on it. The grand plane has an Au (3 μm) sputtered film and Q value of 4,400 (18 K) and 2,800 (77 K) when there are no charges. A Chebyshev three-pole band pass filter was fabricated from the same material and the insertion loss was compared with Au in Figure 10.¹⁷ At temperatures below T_c , the insertion loss is close to Au's 10^{-2} .

5.3 Synthesis of Superconducting Film by MOCVD Method

Studies on the synthesis of superconducting film by the metallo-organic chemical vapor deposition (MOCVD) method is performed from the standpoint of high-speed film fabrication (film growth speed control

Chebyshev Three-pole Band Pass Filters Implemented in Microstripline

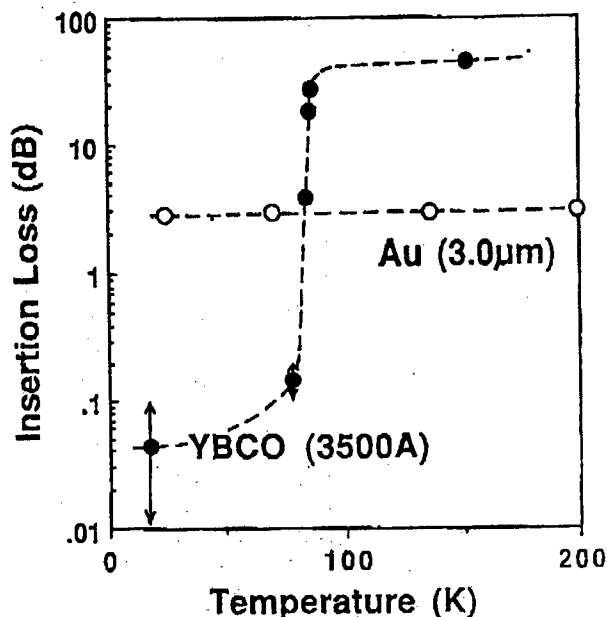


Figure 10. Temperature Dependence of Insertion Loss of Chebyshev Band Pass Filter

over a wide range) and ease of configuration control. Studies on synthesis of superconducting films by the MOCVD method are also recently being studied. BSCCO superconducting film is synthesized onto an MgO(100) single crystal substrate. A T_c value of more than 60 K was observed for superconducting film of average thickness of 3.5 nm. In the case of Sr, Cu, Ca metalloorganic original material, DPM compound and in Bi, organometallic original material like triphenylbismuth were employed. Metalloorganic gas was inserted into the reaction tube filled with Ar as the carrier gas. Metalloorganic gas is mixed with oxygen gas immediately before the reaction tube. Synthesis of the ultrathin film was achieved at a substrate temperature of 750–850°C, total pressure of 10 Torr, and oxygen fraction pressure of 8.8 Torr. Film growth speed was 0.3–3 nm/min. Figure 11 illustrates the relationship between resistance of this ultrathin film and temperature. Films with average thickness of more than 3.5 nm has T_c of more than 60 K while thinner films displayed semiconducting behavior.

This indicates that the superconducting crystal particles of the MOCVD thin film are well coupled when the film whose thickness is equal to the length of the c-axis is assumed to be the boundary. J_c values for a 5 nm ultrathin film under 0 magnetic field is 2×10^5 (A/cm², 4.2 K), 5×10^4 (A/cm², 30 K), and 2.5×10^3 (A/cm², 50 K). When a horizontal field is applied along the film plane, J_c was confirmed to be at least 6 T and independent of the magnetic field. In the future, this ultrathin film synthesis technology will be promoted. Establishment of thin and thick film synthesis techniques will be of the utmost importance.

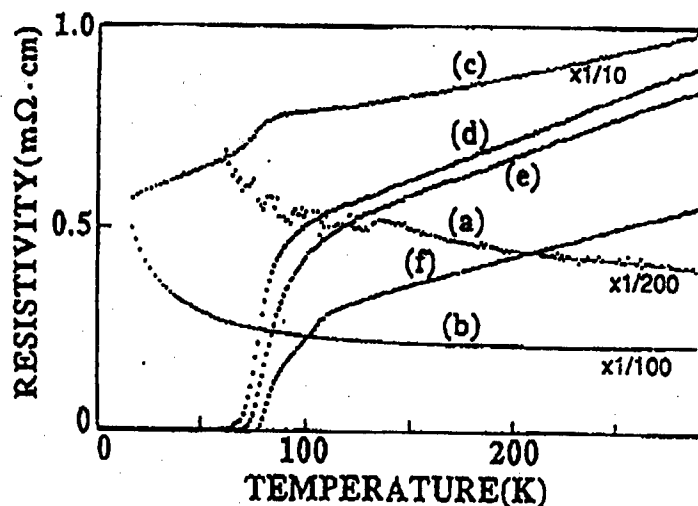


Figure 11. Resistivity Vs. Temperature of (a) 1.7 nm, (b) 2.2 nm, (c) 2.7 nm, (d) 3.5 nm, (e) 5.5 nm, and (f) 11 nm films. Thickness is average value determined by deposition time based on calibrated deposition rate.

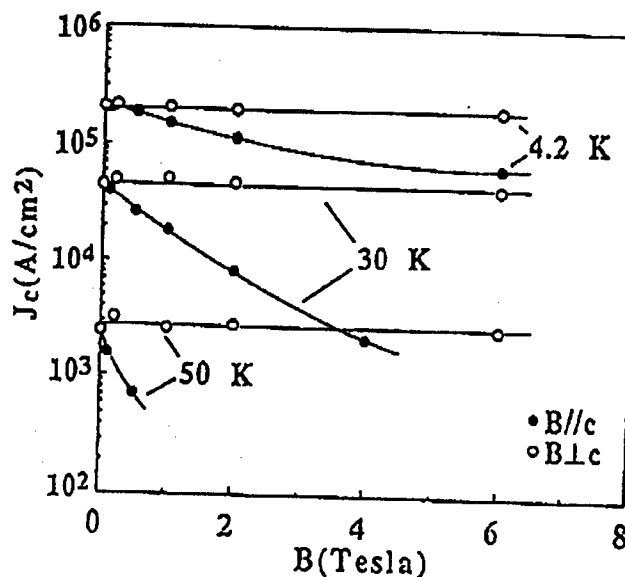


Figure 12. Dependence of J_c on Magnetic Field (Nb: J_c of 5 nm ultrathin film (BSCCO))

5.4 Return to Film Growth Basics

Progress in thin film processes has been striking in the past five years. However, we have bypassed many problems in our hurry to move forward. The thin film fabricated may even have brittle spots in its structure. Tunnel Josephson junctions may be the weak spot in the thin films of today.

5.4.1 Oxygen control

Oxidation or crystallization processes cannot be investigated if oxygen cannot be quantitatively handled in the same manner as metal elements.

When lamination is performed for every (001) atomic plane, the Y-plane in Y-base 123 structure and Ca-plane in Bi-base, respectively, will not include oxygen. Therefore, sputtering in an oxygen environment is impossible. This may be the reason why Ca-plane loses its crystal configuration¹⁸ when every atomic plane in Bi-base is vapor deposited.

5.4.2 Development of substrate material

To realize intraplane arrangement in an a-axis aligned film, the perovskite mixed single crystal lattice arrangement is desirable, Y_2O_3 is a promising substrate for use in microwave devices.¹⁹

Lattice arrangement for $YBa_2Cu_3O_7$ is similar to $SrTiO_3$ and since it is also made of the same constituents, fresh new substrate surfaces can be easily fabricated by homeoepitaxy. The dielectric coefficient is the same as MgO and Al_2O_3 .

References

1. Siegrist, T., et al., NATURE, Vol 334, 1988, p 231.
2. Smith, M.G., et al., Ibid., Vol 351, 1991, p 549.
3. Takano, M., et al., PHYSICA C, Vol 176, 1991, p 206.
4. Roth, G., et al., J. PHYS., Vol 1, 1991, p 721.
5. Cava, R.J., et al., PHYSICA C, Vol 185/189, 1991, p 180.
6. Adachi, S., et al., PHYSICA C, in press.
7. Maeda, T., et al., PHYSICA C, Vol 169, 1990, p 133.
8. Sakai, N., et al., ISS'91 Proceedings, in press.
9. Cava, R.J., et al., PHYSICA C, in press.
10. Kaneko, T., et al., PHYSICA C, Vol 178, 1991, p 377.

11. Tsai, J. S., et al., M²S-HTSC III.
12. Ohata, K., Izumi, H., Hase, T., Suzuki, K., Morishita, T., and Tanaka, S., Material Research Society Symposium Proceedings, Vol 191, 1990, p 183.
13. Izumi, H., Ohata, K., Sawada, T., Suzuki, K., Morishita, T., and Tanaka, S., Proceedings of 3rd International Symposium on Superconductivity, ISS'90, p 1063.
14. Takahashi, H., Hase, T., Izumi, H., Ohata, K., Morishita, T., and Tanaka, S., PHYSICA C, Vol 179, 1990, p 291.
15. Izumi, H., Ohata, K., Sawada, T., Morishita, T., and Tanaka, S., JPN. J. APPL. PHYS., Vol 30, 1991, p 1956.
16. Homma, N., Okayama, S., Takahashi, H., Yoshida, I., Morishita, T., and Tanaka, S., APPL. PHYS. LETT., Vol 59, 1991, p 1383.
17. Suzuki, K., Fujino, S., Takenaka, T., Imai, K., Suginoshta, F., Yamaguchi, K., Ohata, K., Nakao, K., Yazawa, N., Kobayashi, M., Morishita, T., and Tanaka, S., Proceedings of 4th International Symposium on Superconductivity, ISS'91 (in press).
18. Yoshida, I., Kamei, M., Suzuki, K., Morishita, T., and Tanaka, S., APPL. PHYS. LETT., Vol 58, 1991, p 654.
19. Oishi, A., Teshima, H., Ohata, K., Izumi, H., Kawamoto, S., Morishita, T., and Tanaka, S., Ibid., Vol 59, 1991, p 1902.

R&D Trends in Superconducting Devices, Future Issues

926C0071D Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 27-32

[Article by Professor Hayakawa, Engineering Department, Nagoya University]

[Text] 1. Superconductor Electronics: Next-Generation Electronics

It is not an exaggeration to say that advances in semiconductor devices, in particular, silicon large-scale integration (LSI) technology, has supported development of the current electronics industry. Integration of devices increases as silicon technology advances. If silicon integration technology becomes smaller and more integrated, device dimensions will become $0.1 \mu\text{m}$ and integration exceeding 100 Gb by the beginning of the 21st century.

However, most people believe that progress in silicon technology as we move towards the 21st century will not be without problems. There are many issues in silicon technology. First, heat generation is an issue in devices. Heat generation in chips increases with higher integration to speed up devices. Chips used in current high-speed computers consume more than 30 W of energy. Therefore, reduction of power consumption by devices is also a major issue. Lead problems are also becoming acute. Lead resistance increases with downsizing thereby reducing the speed performance of devices. Heat generation by leads will also increase.

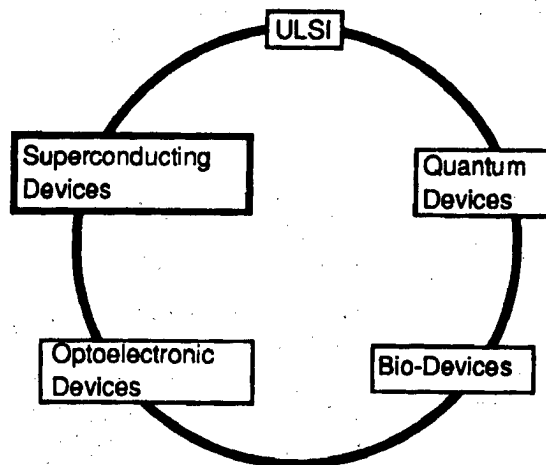


Figure 1. Next-Generation Devices

In this manner, the development of new device technology when silicon technology peaks by the beginning of the 21st century will become very important. Figure 1 illustrates the main next-generation devices that are currently being studied.

Post silicon ultralarge-scale integration (ULSI) is commonly believed to be silicon ULSI. Solutions to the above-mentioned issues in silicon technology may be found and ways to further develop the technology may be developed. Large capacity information processing may even be possible with optical device technologies.

Studies are being performed on new methods to process information by synthetic nerve cells. Tests are also being performed to actively apply quantum mechanic effects that employ the wave nature of electrons in devices.

Of the next-generation device candidates that are currently being studied, superconducting devices are believed to be the most promising and feasible successor to silicon technology.

That is because first, superconducting phenomenon is a macro quantum effect and superconducting devices like Josephson devices, directly apply the quantum effect. This means that, as a device, high performance like speed, sensitivity and precision can be realized. Second, integrated devices like superconducting devices may hold the key to future problems likely to be faced by the above-mentioned silicon integration technology.

Josephson devices operate under power consumption several orders lower than semiconductor devices. This helps to significantly improve the speed of the system that allows a high density of devices to be mounted. Further, the use of superconducting stripline has basically eliminated the lead resistance problem in silicon devices. Since most of the parts have low electric fields, insulation destruction, hot carrier effects, and electromigration effects will not arise. This has already been proved in the Nb-base integrated device recently developed in Japan.

Thus, superconducting devices will hold an extremely important position as the key technology in next-generation electronics.

2. Development of Nb-Base Integrated Circuits

High-temperature superconductors are currently the focus of most research today. In the case of superconductor electronics, development of Nb-base integration technology cannot be ignored. Japan has continued studying the Josephson computer after IBM stopped development in 1983 and has since then produced striking results. Japan replaced the Pb alloy conventionally employed as the material in Josephson devices by an Nb-base material. Today, several thousand gate elements can be mounted. Development of such Nb-base integrating technology helped to increase the integration scale of circuits and thus improve circuit performance. Various prototype microprocessors containing random access memory (RAM), read-only memory (ROM), arithmetic logic unit (ALU), and controllers were fabricated. A computer consisting of Josephson devices was realized. It was experimentally proved that these processors can be operated at clock frequencies of more than 1 GHz.

Results of Japanese development on Nb Josephson integration technology are attracting global attention. These results have stimulated the United States to increase the number of research centers on this technology.

However, Josephson computer technology is still at the experimental stage and many problems must be solved before it can be commercialized. They include packaging technology, coupling technology with the semiconductor system and cooling technology. The solution of these problems will not only be applicable to the Josephson computer but also to future ultrahigh-speed computers. We believe that it is Japan's obligation to complete development of the technology begun. The success of this technology will play an important role in the development of all superconductor electronics including high-temperature superconducting devices that will be developed in the future.

3. High-Temperature Superconducting Devices

The discovery of high-temperature oxide superconductors with T_c exceeding the temperature of liquid nitrogen produced a great impact on the field of superconducting technology. The field of superconductor electronics is considered a large market for high-temperature superconductors.

Studies are currently being conducted on a global scale on applications for various devices. Several devices that may be commercialized in the near future have been reported. Microwave devices or the 77 K operation superconducting quantum interference device (SQUID) are some of the technologies reported in the United States where development is being actively pursued. In Japan, research on three terminal devices with a slightly longer term prospect is being pursued.

We have not reached the stage where we can fabricate devices at will. We are still at the material technology research stage. The main characteristic of high-temperature superconducting material is that the coherence length (several nm) is significantly shorter than metallic superconductors like Nb. It also has very strong anisotropic conductivity. Short coherence length means that the superconductivity of the material is sensitive to crystal arrangement disorder. This requires synthesis of high-quality materials and single crystal thin films for use in devices. However, high-temperature superconductors consist of four to five elements and have complicated crystal configurations. Hence, control cannot be easily achieved. In the future, semiconductor material technology that exceeds the current state-of-the-art will probably be required for device fabrication. Material research must thus be more advanced.

However, high-temperature superconducting thin films are currently being fabricated in many ways and their quality is being rapidly improved. The new heteroepitaxial single crystal thin film technology is steadily being developed for oxide materials with four or five element constituents.

Development of microwave passive parts intensified after high-quality high-temperature superconductor thin films became available. Superconductors have smaller losses in the microwave range when compared with normal metal conductors. Insertion loss is also low thus allowing fabrication of microwave passive parts with high Q values. It also has an advantage over conventional inductive parts because it can be made more compact. Filters, resonators, delay lines and antennas can be easily connected to the superconducting microwave parts by simply marking a pattern onto the superconducting thin film.

R&D in such types of microwave devices are being actively pursued in the United States. One of the major reasons is the high-temperature superconductivity space experiment (HTSSE) project spearheaded by the Naval Research Laboratory (NRL). These devices have been tested in space in the past few years. In the beginning, Japan's response to microwave devices was not enthusiastic but research has increased. Microwave devices have been mainly for applications in the field of satellite communications but, in the future, they are expected to spread to wider fields like mobile communications. High-temperature superconducting devices are currently being viewed as something that can be commercialized in the very near future.

Development of active devices is also vital in the field of high-temperature superconductor electronics. Josephson junctions and three-terminal devices are part of this development.

Development of Josephson junctions is also being actively pursued. The weak Josephson junction device employing crystal grain boundary as the thin film is one of the most successful junctions operating at 77 K developed. Crystal grain boundaries can now be artificially fabricated and arbitrarily placed for use as Josephson junction. Figure 2 shows models of the various methods for artificially fabricating grain boundary Josephson junctions. In the bi-crystal method, two pieces of crystals with differing alignments are stuck together to form the substrate, on top of which a thin film is epitaxially grown to act as the crystal boundary. Next is the bi-epitaxial method where a thin film with differing crystal alignments are grown on a buffer layer and the step method where a step is made on the substrate crystal for junctioning. Finally, there is the edge method where junctioning is done at the edge of the thin film.

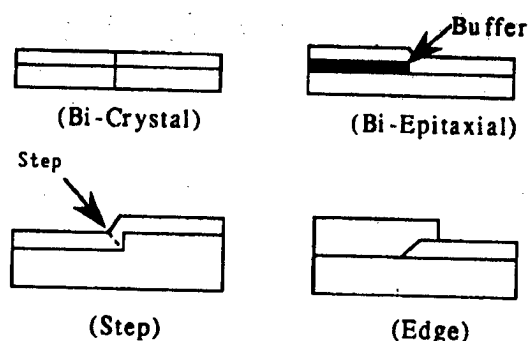


Figure 2. Types of Particle Boundary Bonding

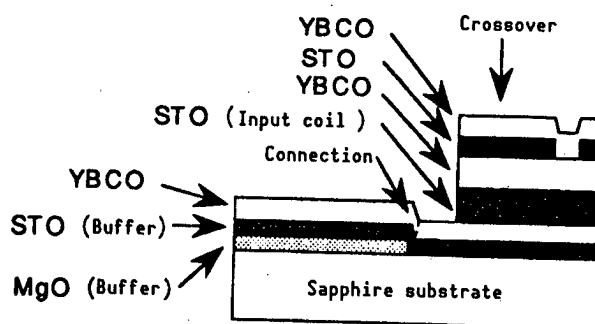


Figure 3. Laminated Structure of Integrated SQUID

Attempts to fabricate devices have already begun with the establishment of thin film and junctioning technologies.

First, SQUID development was spurred. SQUID is made of two Josephson junctions inserted inside the superconducting loop and is employed as a highly sensitive magnetic sensor. Applications include medical equipment and nondestructive inspection equipment like cardiomagnetometers and neuromagnetometers.

The previously mentioned grain boundary Josephson junction is employed for operation at 77 K. A recent success is the integration of pickup coils in the

devices for effective transmission of external magnetic flux to SQUID. In this case, it consists of seven layers of epitaxial thin films. Fabrication technology is also quite advanced. Figure 3 shows the thin film configuration in high-temperature superconductor integrated SQUID.

Japan is actively involved in research on superconducting three terminal devices in an attempt to develop new transistors based on superconducting phenomenon. The repercussion effects of success will be significant. However, its realization cannot be achieved unless highly advanced technologies like fabrication techniques that allow multilayered device structure control or electron state control at boundary surface of thin films must be established. We are still in the basic research stage. The realization of three terminal devices will require some time but it is an issue that must be pursued if high-temperature superconducting device applications are to be expanded. Figure 4 illustrates the structure model for a typical three-terminal device.

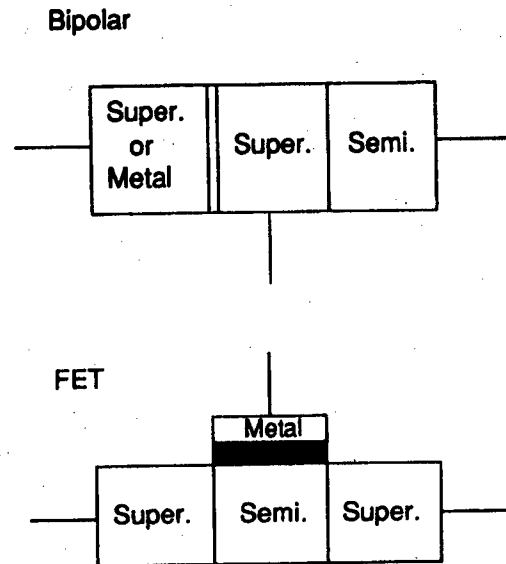


Figure 4. Conventional Tripolar Device

R&D of high-temperature superconducting devices is being conducted in the form of various research ranging from devices that can be commercialized in the near future, like microwave devices and SQUID, to those that require long-term development, like three-terminal devices.

4. Future Policies on Superconductor Electronics

A technology should be realized one by one starting from those that are feasible through market introduction. High-temperature superconducting microwave devices and SQUID will probably be realized in the near future and it is fervently hope that these will become developed into products. Development of these products was spearheaded by the United States, and Japan must step up efforts in developing new applications.

For this reason, development of three-terminal devices will be important as part of Japan's next-generation technology. It is also time to consider applications for these products should they become a reality. The electronics industry has come of age.

Advancement in silicon technology has been particularly remarkable and this cannot be ignored in the future. Ways to link superconducting three-terminal devices with semiconductor devices will become vital. Low-temperature operation of semiconductor integrated circuits like the complementary metal-oxide semiconductor (CMOS) is most likely to become the mainstream in the future and this holds the key to possible development of new device technologies through hybridization of high-temperature superconductor devices and semiconductor devices that complement each other's characteristics.

The introduction of superconductor devices to the maturing semiconductor devices field is an issue that should be seriously considered for further development of next-generation electronics.

Figure 5 summarizes the technical issues and future prospects of superconductor devices.

Technical issues	Devices
High quality thin films High T_c High J_c Low R_s	Microwave devices
Bonding techniques Boundary bonding Thin film lamination	SQUID
Laminated device technology Tunnel bonding Boundary control	Three-terminal device Various devices
Integration techniques Hybridization Mounting technology	Semiconductor-ultraconducting hybrid device

Figure 5. Technical Issues and Devices

Applications, Expectations of Superconductor Industry

926C0071E Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 33-38

[Article by Tsuneo Nakahara, vice chairman, Sumitomo Electric Industries, Ltd.]

[Text] 1. Introduction

High-temperature superconductors were discovered five years ago. During this time, a wide range of research and development studies on high-temperature superconductors that included searches for new materials, explanations for high-temperature superconductivity mechanism, development of processes for thin films and line materials, and applications for devices and magnets, were conducted at the same time on a global scale. Success has also been reported in targeting commercialization of high-frequency devices, large-current conductors, and magnets.

Discovery of high-temperature superconductors has spurred R&D in metallic superconductors and prompted new considerations in applications and evaluations of the total superconductor technology scenario. The status of R&D in superconductors and their application systems as well as future expectations from industry will be described below.

2. Status of Superconductor Application Studies

Development of systems that require superconductors is being carried out over a wide area from power applications to electronics.

Table 1 compares the current development status of various systems in the United States and Japan. A wide range of applications like superconductor devices and SQUID systems in the electronics field, power generators, superconducting magnetic energy storage (SMES) and nuclear fusion systems in power applications, and magnetic levitation trains are included.

Recent advances in Japanese development in superconductor power generators are primary technologies like development of 70,000 kW class low-speed and ultrahigh-speed working models. Development of high-performance line material, increment of current density and reduction of alternating current flow loss

Table 1. Current Application Status of Superconductors

As of December 1991

Application		Metallic superconductor					High-temperature superconductor				
Field	Item	Plan on paper	Basic tests	Feasibility study	Pilot plant	Actual application	Plan on paper	Basic tests	Feasibility study	Pilot plant	Actual application
High energy	Accelerator										
Electric power	Power generator										
	SMES										
	Cable										
	Nuclear fusion										
Transport	Magnetic levitation vehicle										
	Electromagnetic propulsion ship										
Industrial application	S R										
Medical application	M R I										
	SQUID										
Electronics	High-speed device										
	High-frequency device										
	Wiring										

United States

Japan

Prepared by Development and Planning Department,
Sumitomo Electric Industries

have been implemented. Measuring techniques were also developed for heat transmission and insulation characteristics in liquid helium under a severe environment like that in a rotator. New test results on stability were obtained. SMES is an energy storage technique that is highly effective and allows high-speed response. It is a technology that shows various promising effects like load standardization, variable load adjustment, and system stabilization. An extension of the success in tests on the magnetic levitation train on the Miyazaki tracks is the construction of the Yamanashi test track while at the same time development of vital technologies like improvement of magnet reliability and branching are being advanced. Development of nuclear fusion technology is being carried out on an international basis between Japan, the United States, and Europe in the form of a superconductor magnet for heat nuclear fusion test reactors (ITER). Development of the helical method is also smooth with completion of the low-temperature test wing.

The large-scale accelerator, SSC is a U.S. project which uses 10,000 superconductor magnets. Application of these metallic superconductors are propelled

by such large projects as large-scale accelerators and heat nuclear fusion reactors that require international cooperation. These projects can therefore become meaningful prerequisites for future global joint efforts in the large science arena.

High-temperature superconductor application is highly advanced in the United States in high-frequency devices for use in space, while Japan displays strength in line material and power applications. These differences are very interesting.

3. Search for New Materials and Their Theories

The search for new materials was mainly focused on copper oxides like LaBaCuO and LaSrCuO ($T_c = 30\sim 40$ K)¹ in 1986, YBaCuO ($T_c = 90$ K)² in 1987, BiSrCaCuO ($T_c = 80\sim 110$ K)³, and TlBaCaCuO ($T_c = 125$ K)⁴ in 1988, NdCeCuO ($T_c = 30$ K)⁵ in 1989, and C₆₀ ($T_c = 33$ K)⁶ in 1991. The discovery of C₆₀ in 1991 was highly acclaimed for its likelihood of becoming a superconducting material and development of theory for high-temperature superconductivity. Future research for new materials, although difficult to presume, may continue to be a challenging issue judging from the social impact of high-temperature superconductors.

The theory for high-temperature superconductors does not explain what causes the creation of an electron pair. Although powerful theories like the phonon theory and the magnetic field disturbance theory exist, further experimental considerations are expected. Recent interesting reports on cuprous oxide⁷ seem very promising from the standpoint of high-temperature superconductivity characteristic of copper oxides.

4. Power Applications

4.1 Current Development Status of Line Material

Development of high-temperature superconducting line material focused on the three following materials: yttrium base (Y-base),⁸ bismuth base (Bi-base),^{9,10} and thallium base (Tl-base).¹¹ Table 2 summarizes the results obtained for the various bases. Superconducting lines have many applications; large current flow application (around 0.1 Tesla), weak magnetic field magnet application (0.2~1 Tesla), strong magnetic field magnet application (several Tesla), and superstrong magnetic field magnet application (>20 Tesla) are some examples. The superconducting lines at the source of the microgravity in all these applications are required to carry critical current densities of more than 10^4 A/cm². Figure 1 shows the shift of critical current density increment of silver coated Bi-base (2223 phase) superconducting line at liquid nitrogen temperature.

A high-temperature superconductor is anisotropic and requires control at the atomic level. The critical current density at liquid helium temperature, even under the superstrong magnetic field of 23 Tesla, is $103,000$ A/cm² which is significantly higher than that of conventional metal-base superconducting lines. As a result, high-temperature superconducting lines were proved feasible for use over a wide temperature and magnetic field range.

Table 2. Critical Current Density for High-Temperature Superconducting Lead Materials

As of December 1991

External magnetic field	Critical current density J_c (A/cm ²) at 77.3 K			Notes
	0 T	0.1 T	1 T	
Y	4.1×10^3	2.0×10^4	—	Sumitomo Electric
Bi	5.4×10^4	4.3×10^4	1.2×10^4	Sumitomo Electric
Bi (2212)	3.5×10^4	6.0×10^3	4.0×10^2	Furukawa Electric
Tl	2.2×10^4	3.2×10^3	1.1×10^3	Hitachi

Various basic issues like length increment, antidistortion characteristics, and large current conductors are some successful studies on commercialization attempts in the past two to three years. It was proved that 100-m long and multi-core superconductor lead reduces distortion while 1,000 A conductor becomes a compact large-current conductor.

4.2 Development Status of Bulk Material

High-performance bulk material of mainly Y-base type by the fusion method has already been developed. These bulk materials have extremely strong pinning forces even at liquid nitrogen temperatures and are expected to open up new high-temperature superconductor applications like magnetic shields, flywheels, and bearings. Test bearings¹² made of such bulk material were proved capable of 30,000 rpm on a 2.4 kg shaft. Development of such materials also present new perspectives on pinning mechanism at liquid nitrogen temperature which will be very effective for future material development.

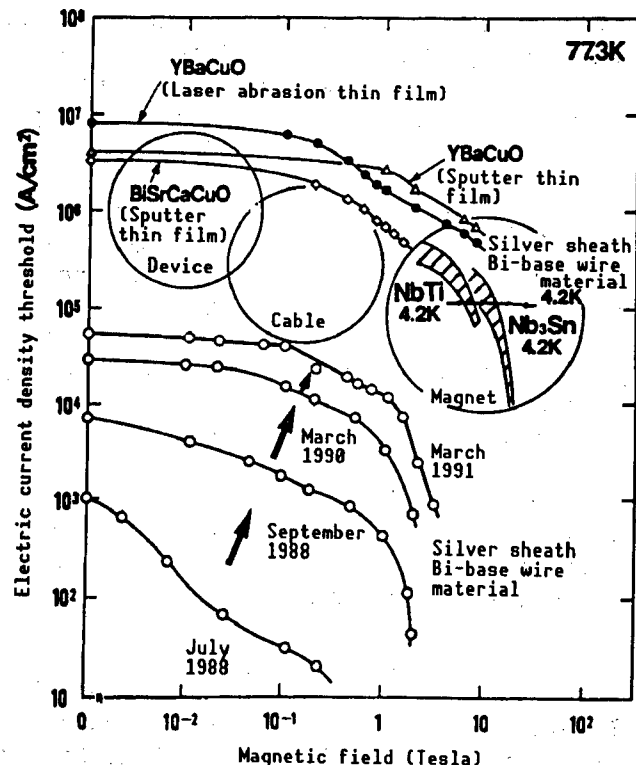


Figure 1. Dependence of Boundary Electric Current Density Threshold on Magnetic Field

4.3 Development of Power Application Systems

Power transmission systems¹³ at liquid nitrogen temperature and superstrong microgravity magnets¹⁴ at liquid helium temperature are some of the proposals made for high-temperature superconductor power application systems. These proposals aim at realizing those areas that were impossible with conventional metal base superconductors but first became feasible with the appearance of high-temperature superconductors. Power transmission systems at liquid nitrogen temperature use conventional ducts for future increased capacity and even when construction of new ducts is difficult, the establishment of economical, yet superior power transmission lines, is an answer to future increasing demands for energy.

5. Electronics Applications

5.1 Development of Electronics Applications Systems

Applications of superconductors in the field of electronics is already a reality in the form of Josephson junctions employing metal base superconducting thin films. Examples include voltage standard with stacks of Josephson junctions and ultrasensitive magnetometer with two ring-shaped Josephson devices. Development of processor and memory elements of the Josephson computer in MITI's large-scale project is also under way. The results of this project were applied by the Electrotechnical Laboratory in the prototype Josephson calculator and by the Fujitsu Research Institute in the prototype calculator employing Si and Josephson chips. The Superconductor Sensor Research Institute under the Japan Key Technology Center was established in 1990 to make contributions to medicine and clarify the functions of the brain through measurements of the infinitesimally weak magnetic field generated by the brain. The development of a superconductor magnetic sensor system for measuring the biological magnetic field in 200 ch of living organisms is now under way.

The so-called dream device called Josephson device is already in use in some fields as described previously. They show a high potential as the market products and research are being actively pursued. Superconductors are expected to revolutionize the structure of the electronics field.

5.2 High-Temperature Superconductor Electronics

Before high-temperature superconductors can be applied in the field of electronics, thin film technology is a vital requirement. For this reason, the development of thin films is currently being vigorously pursued after the initial discovery of high-temperature superconductors. There are already studies on the fabrication of thin films from typical high-temperature superconductors like Y-base, Bi-base, and Tl-base. One of the results is a thin film with critical current density of 10^6 A/cm^2 at liquid nitrogen temperature reported in 1989.

One application of thin films is the Josephson device and because of the extremely short coherence length in high-temperature superconductors,

fabrication of a laminated metal base superconducting thin film becomes very difficult and thus, a superconductor-insulator-superconductor (SIS) junction with superconductor/insulator/superconductor structure is still not available. However, fabrication of a superconductor/noninsulator/superconductor (SNS) junction with an electrical conductor as the middle layer has been reported. A superconducting current flow over a long distance in hitherto unbelievable nonsuperconducting layer (long-distance neighboring effect) was also reported¹⁵ and clarification of that phenomenon and its application in devices looks promising.

It is now understood that the so-called weak Josephson junctions are relatively easy to fabricate and thus, development of SQUID that use such junctions is well under way. Studies are also being done on measurement of quantum magnetic flux, noise reduction, and magnetic flux transformer combinations.¹⁶ Such SQUID exhibit potential use in biological magnetometers as well as a wide range of other applications like nondestructive analysis and resource inspection.

Studies are being done on the application of high-temperature superconducting thin films in microwave and milliwave parts because its surface resistance to high frequencies is about 1-2 order smaller than metals. Prototypes of high-performance resonators, filters, and antennas are now available.¹⁷ Applications to satellite broadcasting equipment are currently under study.

The Next-Generation Project (Jisedai) since 1988 aims at the fabrication of a three-terminal device that operates under the new principles of the high-temperature superconducting thin film. Basic studies and new structure proposals¹⁸ were made for the three-terminal devices which show great promise as ultrahigh-speed multifunctional arithmetic logic devices for use in the central unit of the 21st century computer.

6. Future Prospects

Steady progress is being made in the development of applications in the field of superconductors like metal-base superconductors and high-temperature superconductors, as described above. Superconductor technology is believed to be the key to future industry for both the energy and electronics sector. This is the reason for continued research efforts. In particular, high-temperature superconducting line material is the key to development of power transmission systems and electrical power equipment in the field of energy. This is a vital development issue from the standpoint of Japan's energy supply in the 21st century.

Together with the challenge in developing high-temperature superconductors, it is also fervently hoped that studies to fully use such materials will also be conducted with vigor.

References

1. Bednortz, J.G. and Muller, K.A., Z. PHYS., Vol B64, 1986, p 189.
2. Wu, M.K., Ashburn, J.R., and Chu, C.W., PHYS. REV. LETT., Vol 58, 1987, p 908.
3. Maeda, H., Tanaka, Y., Fukutomi, M., and Asano, T., JPN. J. APPL. PHYS., Vol 27, 1988, p L209.
4. Sheng, Z.Z. and Hermann, A.M., NATURE, Vol 332, 1988, p 138.
5. Tokura, Y., Takagi, H., and Uchida, S., Ibid., Vol 337, 1989, p 345.
6. Hebard, A.F., et al., Ibid., Vol 350, 1991, p 600.
7. Masumi, T., J. PHYS. SOC. JPN., Vol 60, 1991, p 3625.
8. Mukai, H., et al., "New Developments in Applied Superconductivity," ed. by Y. Murakami, World Scientific, Singapore, 1988, p 101.
9. Ueyama, M., Hikata, T., Kato, T., and Sato, K., JPN. J. APPL. PHYS., Vol 30, 1991, p L1384.
10. Uno, N., et al., "Advances in Superconductivity II," ed. by T. Ishiguro and K. Kajimura, Springer-Verlag, Tokyo, 1990, p 341.
11. Seido, M. and Kamo, Y., ISTEJ JOURNAL, Vol 4, 1991, p 42.
12. Fukuyama, H., et al., submitted to Proceedings of 4th International Symposium on Superconductivity, Tokyo, 14-17 Oct 1991, (ISS'91).
13. Hara, T., Okaniwa, K., and Yamamoto, T., "Advances in Superconductivity II," ed. by T. Ishiguro and K. Kajimura, Springer-Verlag, Tokyo, 1990, p 1059.
14. Sato, K., et al., J. APPL. PHYS., Vol 70, 1991, p 6484.
15. Tarutani, Y., et al., 10th Symposium on Future Electron Devices, Tokyo, 21-22 Oct 1991.
16. Lee, L.P., et al., APPL. PHYS. LETT., Vol 59, 1991, p 3051.
17. Higaki, et al., Sumitomo Electric Industries, Ltd., Vol 140, 1992, to be published.
18. Kamigaki, Y., 10th Symposium on Future Electron Devices, Tokyo, 20-21 Oct 1991.

Results of Three Studies on High-Functional Polymer Materials

926C0071F Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 41-46

[Article by Junji Kaeriyama, chairman, Research Institute for Polymers and Textiles]

[Text] 1. Introduction

The Next-Generation Project was established in 1981. Under this project, the 10-year study on highly effective polymer separation membrane material, conductive polymer material, and highly crystalline polymer material which began in FY 1981, terminated in FY 1990. An overview of the results of this 10-year study is given below.

2. High-Efficiency Polymer Membrane Separation Material

2.1 R&D Requirement

In all industries including the chemical industry, separation processes for matter are extremely important. Separation by membrane consumes very little energy when compared to conventional separation methods like the general distillation method. Operation is simple, the separation device can be made more compact, and automation can be easily achieved. Development of the separation membrane was deemed essential for the alcohol, petrochemical, fine chemical industries as well as for matter which is unstable when heated thus making conventional separation and refinement methods difficult. Separation membranes are also developed from the standpoint of conservation of resources and pollution prevention.

2.2 Organizations In Charge

National Research Laboratories:

Chemical Technology Laboratory
Research Institute for Polymers and Textiles
Product Science Laboratory

Laboratory consortium: Asahi Kasei Kogyo, Asahi Glass, Kurare, Sumitomo Denki Kogyo, Daiseru Kagaku Kogyo, Tiejin, Toyo Boseki, Toray, Mitsubishi Kasei

2.3 Overview of R&D

The following are studies that produced results which exceeded world standards:

(1) Polyhydric of polyion treated water selective permeable membrane for concentrating water-alcohol solutions

These are the chitosan separation membrane treated with sulfuric acid and the polyacryl acid separation membrane obtained from hydrolysis and treated with polycation and made into complex polyion. These are hollow complex membranes. The actual separation membranes were actively implemented in the outsourced research and investigation project by the Alcohol Monopoly Corporation and is currently being investigated in a benchplant. This is the first time in the Next-Generation Project that a commercial benchplant was constructed.

Continuous production and concentration of ethanol by the fermentation method is achieved by combining this result with the alcohol selective permeable membrane studied under another research theme.

(2) Water selective permeable membrane for separating acetic acid/polar organic water solvent solution

The performance of polyparaffin acid nonsymmetrical membrane for acetic acid-water solution is superior while for typical polar organic solutions like N,N-dimethylformaldehyde-water solution, the iron (III) chloride ion bridged copolymerized tetrafluoroethylene/hydroxymethylene membrane displays excellent separation characteristics. This membrane was proved durable and stable for more than one month.

(3) Amino acid optical resolution membrane using chiral crown ether

Various types of d, l-amino acid supporting type infiltrated liquid membranes that are stable and porous with separation ratios exceeding 10 and are capable of optical resolution transportation were developed from the new chiral crown ether.

Porous membranes like cellulose nitrate and membrane solutions like O-nitrophenyloctylether were proven stable for more than 15 months.

Success was reported on amino acid concentrations by the granular separation method using the liquid membranes. Amino acid concentration can be effectively performed after the amino acid resolution membrane is combined with d,l resolved from synthetic amino acid.

(4) Liquid membrane with carrier for separating carbon monoxide/nitrogen, oxygen/nitrogen

Superior separation was observed in liquid membranes containing copper chloride/N-methylimidazole carrier for separating carbon monoxide/

nitrogen and sacosine base or histidine base cone-shaped carrier for separating oxygen/nitrogen.

Only excellent results are described below:

(1) Plasma surface treatment separation membrane

A liquid separation membrane was fabricated by plasma surface treatment and at the same time, polymerization conditions for hydrophilic and hydrophobic monomers were also studied. The relationship between water and alcohol selective permeability was also observed to determine the various factors involved in membrane fabrication.

A permeable mechanism was also studied through a proposal for measuring the concentration distribution of transmitted matter within the membrane. In this manner, a general index was established for membrane fabrication.

(2) Study on nonsymmetrical membrane by phase transition method using aromatic polyimides

For the first time, a separation membrane solute exhibiting reverse osmotic levels was developed from nonwater soluble liquid. Conjugated membranes were then fabricated by the vapor deposition polymerization method using the above as base membranes. A new dry, conjugated membrane fabrication technique was developed by using solvent-resistant polyimide conjugated membrane.

(3) Discovery of grainy structures in hydrophobic solid membrane and new proposal for permeability mechanism

Hydrophobic membranes like poly(1-trimethylsilyl-1-propene), polyacrylonitrile (PAN), and polyfluorovinylidene was found to be made up of minute solid polymer grains. The pores within the solid structure were proven to play an important role in the separation process.

(4) Clarification of permeability and sorption phenomena in compressed polymer in glass state

An expanded two-dimensional sorption equation was proposed for explaining the plasticization (isothermal gas transition) and sorption phenomena during gas concentration in the polymer in its glass state.

(5) Explanation for deterioration mechanism in membrane containing carrier for separating oxygen/nitrogen--stability improvement

Solid or liquid membranes containing complex shaped carriers suffer from deterioration of the carrier shapes. Studies to explain the deterioration mechanism and regeneration methods are made.

Stability was also improved through carrier structure control.

3. Polymer Conductors

3.1 R&D Requirement

Metallic material is rollable and malleable but requires a large amount of energy for smelting and is weak to corrosion and rust. Polymer conductors excel over metal conductors as they are corrosion resistant, lightweight, and very workable. As the performance and integration of electronic and electrical equipment become more advanced, the demand for newer and better materials with more diverse properties becomes stronger. A polymer conductor and organic superconductor are currently the focus of a lot of attention in this area. Japan must actively pursue R&D in this field.

3.2 Organizations in Charge

National Research Institutes:

Research Institute for Polymers and Textiles
Electronic Technology Research Institute

Consortium: Asahi Kasei Kogyo, Sumitomo Kagaku Kogyo, Sumitomo Denki Kogyo, Teijin, Toray.

3.3 Overview of R&D Results

Results exceeding world standards in electrical conductivities are listed:

(1) Synthesis conditions for polyacetylene were conducted. A film with conductivity of $4 \times 10^5 \text{ A/cm}$ was fabricated and the high conductivity generation mechanism was clarified.

(2) A poly.4-phenylene vinylene synthesis method was developed from the sulfonium salt dissociation method and a fiber exhibiting conductivity of $2.7 \times 10^4 \text{ S/cm}$ was fabricated.

(3) A polypyrrole film with a conductivity of $3 \times 10^3 \text{ S/cm}$ was synthesized by improving electrolytic polymerization and drawing methods.

(4) By doping the graphite thin film fabricated by the electrical discharge laminated polymerization method, with AsF_5 , conductivity of $9 \times 10^5 \text{ S/cm}$ was achieved.

(5) The normal pressure organic superconductor $(\text{TMTSF})_2\text{ClO}_4$ single crystal was first grown. Measurements of the critical magnetic field and tunnel effect, has proved this material to possess very strong anisotropic superconductivity. Then, $\beta\text{-(BEDT-TTF)}_2\text{I}_3$ single crystal that displayed superconductivity of 1.2 K, and grown under normal pressure, was proved to exhibit the world's strongest superconductivity of 8 K when under pressure. In this manner, the transition temperature (T_c) of organic superconductors was significantly updated.

Next, we will list those basic studies that gave excellent results.

(1) Substitution of the polythiophane and polypyrrole base created a new soluble conducting polymer whose correlation between its structure and characteristics were clarified through systematic synthesis.

(2) Clarified intra- and intermolecular conductivity mechanism in poly-P-phenylene fluoride that possess nonconjugated chain structure and in highly malleable polyacetylene.

(3) Epitaxial polymerization of acetylene on benzene crystal surface or laminated LB membrane with alternate layers of bimolecular bi-substituted diacetylene and mobile TTF-TCNQ complex charges.

(4) Various studies to stabilize conductivity: Deterioration mechanisms and ways to stabilize material through coating and use of inert environment.

(5) Grow β -(BEDT-TTF)₂ trihalide base complex crystals and identified superconductivity through weak localized Anderson effect. Successfully observed the Shubnikov-de Haas effect, Dohass-Fanalfane effect, and Hall effect in various (BEDT-TTF)₂X salts thereby helping us to understand Fermi surface or electron structure of organic metals.

4. Highly Crystalline Polymer Material

4.1 R&D Requirement

Polymer materials are very workable as well as being lightweight. Highly crystalline polymer material is extremely strong, elastic, and corrosion resistant and is, therefore, very promising as an epochal, new material for replacing metallic materials for use in mechanical parts. The very reliable, lightweight and highly crystalline polymer materials already commercially employed are iron and aluminum. These replacement materials are also very important from the standpoint of energy and resource conservation and must therefore be developed without delay.

4.2 Organizations in Charge

National Research Institute:

Research Institute for Polymers and Textiles

Consortium: Asahi Kasei Kogyo, Teijin, Toray, Mitsubishi Kasei, Mitsubishi Yuka

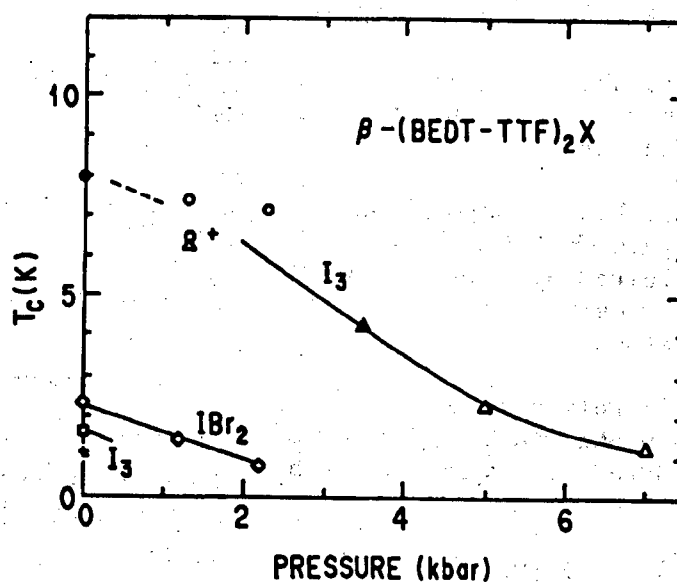


Figure 1.

4.3 Overview of R&D Efforts

The following are results that have reached world standards.

(1) Liquid crystal polyallylate sheets or sticks fabricated by injection molding method or rolling flow method.

(2) Polyimide or polyimide benzohistiasol film or laminated sheets fabricated by the wet molding method.

(3) Polyazometheneamide sticks fabricated by magnetic field arrangement molding method.

(4) Poly-P-phenylenebenzohistiasol/aramide copolymer molecule compound film or fused deposition laminated sheet fabricated by wet molding method.

For isotropic materials:

(1) Under high temperature and pressure, polyacrylic acid base three-dimensional metal salt bridge can be fabricated by compression molding.

(2) Diacetylene base three-dimensional bridge can be fabricated by either solid phase polymerization under high temperature and pressure or by liquid phase polymerization under high temperature, normal pressure.

Favorable results of basic studies are as follows:

(1) Very hard polymer with multidimensional networks fabricated from solid phase polymerization of diacetylene nylon salts.

(2) Proposal of very effective structure evaluation method for surface regularity of extruded liquid crystal polyester sheet with the help of polarized reflection spectrum or identification of vibration spectrum shift in polyoxymethylene with differing crystal structures.

5. R&D Results

Table 1 summarizes the official research results which have also been presented at nine next-generation symposiums.

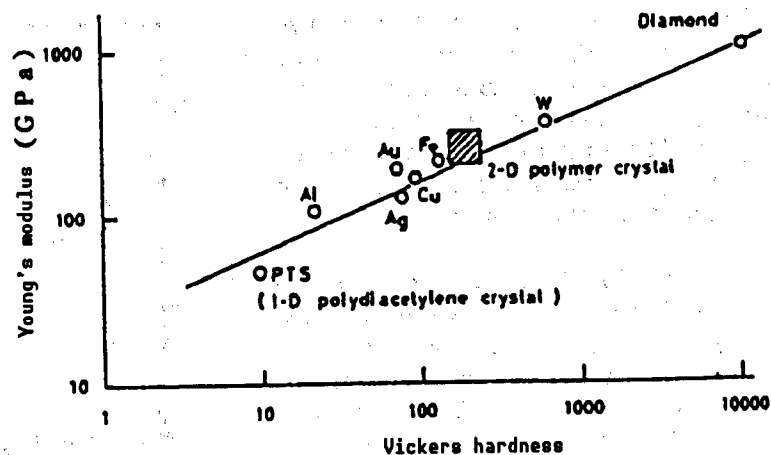


Figure 2. Relationship Between Young's Modulus and Vickers Hardness for Crystalline Materials

Table 1. Official Research Results

	Verbal/ lecture	Paper *1	Expla- nation	News- paper	Domestic patent*2	Inter- national patent*2
High efficiency polymer separation membrane material						
National research institutes	314	73 (37)	57	18	61 (20)	6 (4)
Consortium	100	19 (6)	6	0	180 (23)	21 (10)
Conductive polymer material						
National research institutes	519	243 (221)	64	22	38 (16)	5 (4)
Consortium	146	66 (53)	6	10	129 (25)	27 (18)
Highly crystalline polymer material						
National research institutes	124	41 (29)	14	0	10 (4)	1 (1)
Consortium	98	43 (4)	9	3	238 (17)	11 (7)
Total	1,309	495 (350)	156	55	656 (105)	71 (44)

Notes: *1: Figures within parentheses indicate papers written in English.

*2: Figures within parentheses indicate existing or reported cases.

R&D on Silicon-Based Polymer Material

926C0071G Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 47-52

[Article by Masato Tanaka, manager, Hetero-Element Chemistry, Precision Chemistry Department, National Chemical Laboratory for Industry]

[Text] 1. Introduction

In 1949, Burkhard, et al., first synthesized what we today call polysilane. It is a high polymer compound with silicon as the main element chain.

This initial polysilane with high molecular weight is unfortunately exceptionally insoluble and thus temporarily disappeared from the development scene. In the mid-1970s, however, Japan restarted R&D on carbonified silicon fibers. A soluble and workable polysilane was successfully synthesized by the University of Wisconsin and the UCC Corporation around 1980. A silicon analog with an organic chemical structure similar to that of ethylene was isolated. This area became increasingly active as the following functions were identified.

2. Silicon-Based Polymer

The principal chain of silicon-based polymer material is partially or wholly made up of silicon elements. Silicone with silicon and oxygen in its principal chain is also in this category. In addition to silicone, there can be a silicon-based polymer with the structure as shown in Table 1. These are basically organic-inorganic hybrids and if silicone is assumed to be an organic mineral with an organic base covering the primary structure of its silicate salts, then polysilane is an organic metal with an organic base attached to the primary structure of metallic silicon. Silicon polymer is polymerized from various organic and inorganic polymers. Some of them are listed in Table 1.

The basic reactions in these synthesis techniques are still under study but they can be roughly classified into those listed in Table 2.

The chemical and physical properties of silicon-based matter and material is summarized as follows:

Table 1. Silicon High Polymer Classification (Except silicone)

Classification	Basic structure/typical structure
Ladder silicone	$\left(\begin{array}{c} \text{SiR-O} \\ \\ \text{O} \\ \\ \text{SiR-O} \end{array} \right)_n$
Polyborosiloxane	$\left\{ \text{SiR}_2\text{-O-B} \begin{array}{c} \text{O} \\ \diagup \end{array} \right\}_n$
Polysiloxane	$\begin{array}{c} \text{MeSiH-NH} \\ \quad \\ \text{N} \quad \text{SiMe} \\ \quad \\ \text{SiMe} \quad \text{N} \\ \quad \\ \text{NH-SiHMe} \end{array} \right)_n$, $\left(\begin{array}{c} \text{SiH-NH} \\ \\ \text{NH} \\ \\ \text{SiH-NH} \end{array} \right)_n$
Polycarbosilane	$\left\{ \text{SiHMe-CH}_2 \right\}_n$, $\left\{ \text{C}_6\text{H}_4\text{-SiMePhSiMePh} \right\}_n$
Polysilane	$\left\{ \text{SiMe}_2 \right\}_n$, $\left\{ \text{SiPhMeSiMe}_2 \right\}_n$, $\left\{ \text{SiR=SiR} \right\}_n$ $\left(\begin{array}{c} \text{SiR} \\ \\ \text{SiR} \end{array} \right)_n$, $\text{R-Si} \begin{array}{c} \text{X} \\ \end{array} \right)_n$
Silyl organic polymers	$\left\{ \text{CH}_2\text{CH} \begin{array}{c} \\ \text{SiH}_3 \end{array} \right\}_n$, $\begin{array}{c} \text{Me} \\ \\ \text{C}=\text{C} \\ \quad \\ \text{SiMe}_3 \end{array} \right)_n$
Others	$\left\{ \text{N} \begin{array}{c} \text{CO} \\ \diagup \end{array} \text{Ar} \begin{array}{c} \text{CO} \\ \diagdown \end{array} \text{N} \text{C}_6\text{H}_4\text{-SiMe}_2\text{SiMe}_2\text{-C}_6\text{H}_4 \right\}_n$ $\left(\begin{array}{c} \text{O} \\ \\ \text{O-Si} \end{array} \right) \text{Organic polymer} \left(\begin{array}{c} \text{O} \\ \\ \text{O-Si} \end{array} \right)_n$

(1) Although it is a typical inorganic element, it can be fabricated into a substance with the same basic structure as organic compounds. Bonds in Si-Si, Si-H, and Si-halogen are highly reactive chemically when compared to its carbon compound. Consequently, various organic and inorganic hybrid materials can be fabricated by applying organic chemical methods in molecular engineering.

(2) The σ electron in Si-Si bond has the same energy level as the π electron in C-C bond. Neighboring Si-Si bonds also conjugate very easily. Consequently, all the physicochemical features observed in unsaturated conjugated organic polymers can be realized in saturated polysilane.

Table 2. Synthesis Methods for Silicon Polymer

Reaction	Reaction equation
Halogen removal condensation	$\text{SiR}_2\text{Cl}_2 \longrightarrow \{\text{SiR}_2\}_n + \text{Cl}^-$ $\text{ClR}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiR}_2\text{Cl} \longrightarrow \{\text{SiR}_2\text{SiR}_2-\text{C}_6\text{H}_4\}_n + \text{Cl}^-$
Hydrogen removal coupling	$\text{SiH}_2\text{R}_2 \longrightarrow \text{H}_2 + \{\text{SiR}_2\}_n$
Ring opening polymerization	$\begin{array}{c} \text{Me}_2\text{Si}-\text{CH}_2 \\ \\ \text{H}_2\text{C}-\text{SiMe}_2 \end{array} \longrightarrow \{\text{SiMe}_2\text{CH}_2\}_n$ $\begin{array}{c} \text{Me}_2\text{Si} \\ \\ \text{C}_6\text{H}_4 \\ \\ \text{Me}_2\text{Si} \end{array} \longrightarrow \{\text{Me}_2\text{Si}-\text{C}_6\text{H}_4-\text{SiMe}_2\}_n$ $\begin{array}{c} \text{Si} \\ \\ \text{Me}_2 \end{array} \text{ (in cyclopentane ring) } \longrightarrow \{\text{CH}=\text{CHCH}_2\text{SiCH}_2\}_n$
Masked disilenes Anion polymerization	$\begin{array}{c} \text{MeRSi}-\text{SiMeR}' \\ \\ \text{Ar}-\text{C}_6\text{H}_4 \end{array} \longrightarrow \text{ArPh} + \{\text{SiMeRSiMeR}'\}_n$
Hydrosilyl polymerization	$\text{HC}\equiv\text{CH} + \text{SiH}_4 \longrightarrow \{\text{SiH}_2\text{CH}_2\text{CH}_2\}_n$

(3) Bonds between silicon and heteroelements like oxygen or nitrogen are thermally stable. Bonding energy with carbon is equal to that between carbon-carbon. Consequently, fabrication of a highly heat-resistant polymer looks promising.

3. Functions and Physical Properties Anticipated

(1) Conductivity

West, et al., observed conductivity in AsF_5 doped polysilastyrene made by substituting the principal carbon chain in polystyrene with silicon and the subchains of hydrogen with a methyl base. Conductivity was raised to 10^9S/cm through bridging by light irradiation. Matsumoto, et al., expanded observations to polysilane which contains germanium atoms in its principal chain. On the other hand, Ishikawa, et al., synthesized and evaluated for conductivity, various sigma- π conjugated polymers with alternate Si-Si bond and carbon unsaturated bond (phenylene, vinylene, ethylene, etc.).

The conductivity mechanism is currently still unclear and measured maximum values only reached orders of 10^9 . The main focus is the fabrication of polysilane whose conductivity exceeds that of metal by introducing higher polymerization orders.

(2) Photoconductivity

Polysilane exhibits photoconductivity as a result of the hole created by incident light. Holes move at a speed of $10^{-4} \text{ cm}^2/\text{V}/\text{sec}$, an extremely high value for a single polymer material when compared to the 10^{-7} order in commercial organic photosensitive substances like polyvinyl carbazole. Studies are therefore done on the use of polysilane holes in electron photographs.

(3) Nonlinear Optical Materials

Tertiary nonlinear optical materials will be applied in optical computers and are also being studied in the Next-Generation Project. The π -conjugated polymers are also being considered for use as organic materials.

The sigma conjugated polymer-, polysilane-, is a very promising substance as it is transparent particularly in the visible spectrum. Values of the order of 10^{-12} esu at 1064 nm have been reported.

(4) Chromism

Polysilane with long chains of organic bases display thermochromism when in the solid or liquid state depending on the position of its molecules. For example, (SiHex^2) thin film absorbs ultraviolet light having a wavelength of 316 nm when above 42°C , or 374 nm when below. Similar absorption can be generated by changing the pressure; for instance, 374 nm absorption even above 42°C results when under several thousand atmospheric pressure.

(5) Photoresist Material

Si-Si bonds in polysilane or poly (phenylene-disilanylene) are broken by incident ultraviolet light thus allowing it to be employed as a positive type photoresist. A thin film of SiO_2 is generated on the surface of the light-exposed pattern resist during dry etching by oxygen plasma. This thin film acts as an etching barrier. As a result, the conventional three-layer resist containing SiO_2 layer can be altered to a two-layer resist by removing the SiO_2 layer.

(6) Material With Heat-Resistant Structure

Materials containing silicon include the flexible organic silicon polymer with low internal rotating potential that is similar to silicone, low glass transition and melting points, difficult to mold and not very tough and the inorganic silicon oxide, carbide or nitride that has superior heat resistance and rigidity. Various hybrid materials with in-between properties exist. For example, between silica and silicone, ladder polysiloxane whose thermal dissociation temperature exceeds 500°C , exists. The heat resistance of this material can be improved by controlling the molecules of the organic branches.

The internal rotating potential of molecules in polycarboxilane and polysilazane is higher than that in silicone. Since bridging density can be increased with carbon or nitrogen, their thermal and mechanical properties can be advantageously designed. Such organic-inorganic hybrid materials will be important future issues and are potential fillers of the blank area between existing engineering resins and ceramics.

Phase/fiscal year	Phase One					Phase Two		Phase Three		
R&D theme	3	4	5	6	7	8	9	10	11	12
Development of molecule design and synthesis technology	Research and development of molecule design techniques and molecule structure control techniques →					Improvement of molecule design and molecule structure control →		Establishment of molecule design policies and molecule structure control →		
Molecule design and molecule structure control										
Monomer and polymer synthesis										
	Research and development of monomer and polymer synthesis techniques →					Improvement of monomer and polymer synthesis methods →		Optimization of synthesizing method and establishment of overall manufacturing process →		
	Research and development of material fabrication techniques →					Improvement of material fabrication techniques →		Establishment of material fabrication techniques →		
Development of material fabrication technology								Material optimization →		
	Research and development of structure analysis techniques and raw material and material evaluation techniques →					Establishment of structure analysis & material evaluation methods →		Evaluation of properties of raw material and material →		
Development of evaluation techniques										

Figure 1. R&D Scheme for Silicon Polymer Material

4. Overview of R&D Project on Silicon-Base Polymers

This project aims at realizing conductors, semiconductors, and other materials made of silicon polymer with superior heat resistance, incombustibility, and strong mechanical strengths based on the aforementioned silicon characteristics. The project will be conducted according to the flow chart in Figure 1. Fabrication of diverse biological substance groups was achieved by passing organic compounds in a current of gaseous carbon dioxide. On the other hand, solid silicate salt minerals are almost nonbiological and since organic silicon compounds are basically artificial substances, the research and development of new materials and synthesis technology requires much effort.

The main study items are listed below:

- Molecule design: Molecular weight, principal chain structure, side chain structure, relationship between functions and properties of two-dimensional and three-dimensional structures
- Monomer synthesis technique: Hydrosilane, halosilane, ring monomer, sililene, silane, di-silane
- Development of polymerization reactions: Wurtz method, dehydrogenation coupling, anion polymerization, ring-opening polymerization, hydrosilyl polymerization, electrolytic polymerization, gaseous phase reaction, etc.
- Material fabrication technique: Function enhancing and improvement through bridging, IPN molding, thin film fabrication and doping.

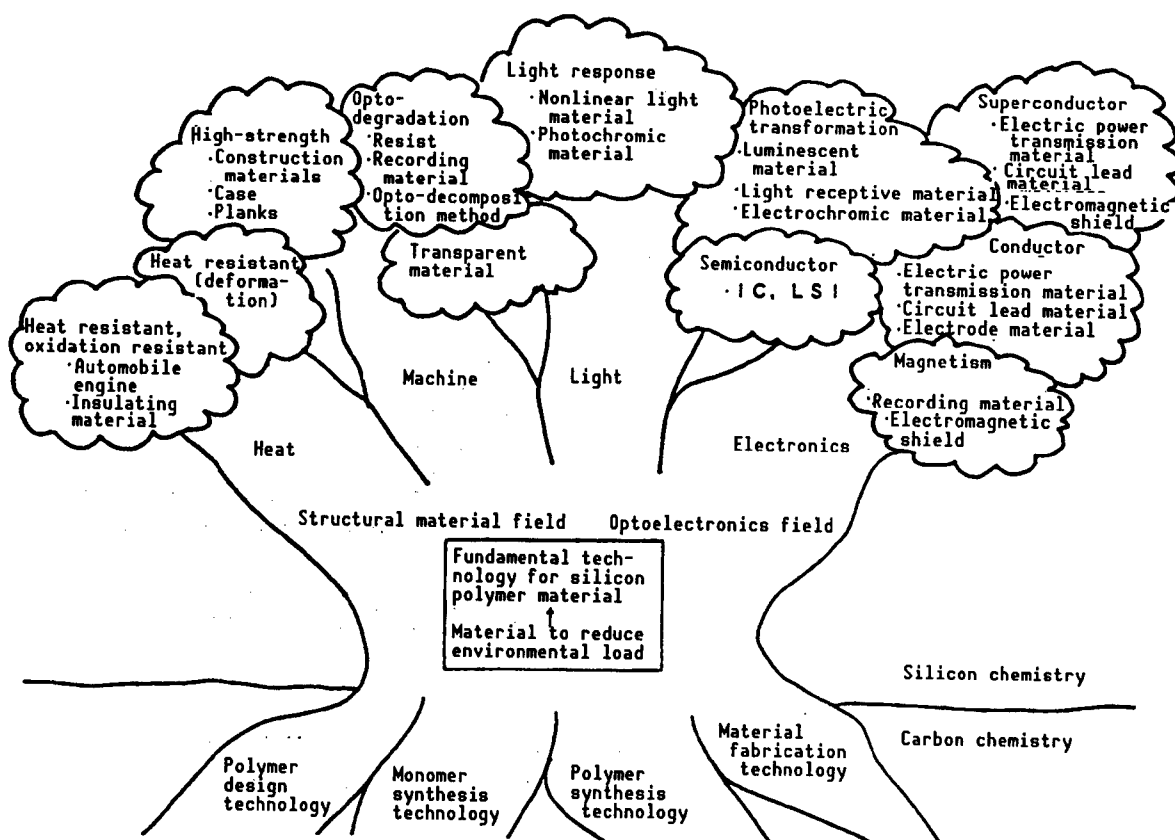


Figure 2. Potential Applications for Silicon Polymer Material

5. Conclusion

R&D on silicon polymer material which began in FY 1991 will mature in the next fiscal year. The history of research in organic silicon chemistry is still young and is nowhere near that of organic chemistry in extent and depth. The two barriers in the form of research for synthesis methods as well as discovery and improvement of functions will be difficult to overcome. However, as shown in Figure 2, technical fields influenced by silicon chemistry is far and wide. Its potential contribution to biocompatible material, medicinal drugs, agricultural drugs and precision synthesis will be the future focus. It is hoped that technical procedures can be established through advice on all aspects.

R&D in Photosensitive Materials

926C0071H Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 55-60

[Article by Masahiro Irie, professor attached to Functional Substance Science Laboratory, Kyushu University]

[Text] 1. Introduction

There is a strong demand for significant improvement in the quality and quantity of information processing related equipment for handling increased information. Information recording equipment is the main focus and issues like higher recording speeds, higher density, and larger recording capacity have surfaced. Currently, the main recording method is magnetic and its recording density has almost reached capacity. One promising way of overcoming this limit is by the use of lasers.

Studies on photosensitive material are therefore based on this history and aims at developing fundamental techniques for control of molecular configurations through light effects, ultrahigh density recording, and high-resolution displays, and for use in optical switches. The results of these studies will not only be applied in optical recording but are expected to spread to all photonic devices in the forthcoming age of light.

2. Current Status of Optical Recording Material

The importance of optical recording was triggered by the spread of read-only CDs and VDs (LDs). CD production topped 185 million per year while LD is 20 million per year. CD-ROM for use in personal computers has already been commercialized and this has led to electronic publishing. Together with the read-only disks, add-on optical disks also became popular with a drop in retail prices. Optomagnetic disks were commercialized in 1989. Standardization is also well under way. Add-on disks that satisfy CD specifications are also being developed.

During optical recordings light energy is converted into heat energy (heat mode recording) except for the add-on and rewritable type. As a result, the various basic light characteristics like wavelength, phase and polarization are not fully employed in the recording process. The recording density becomes

limited if this heat mode is employed since only the pit structure can be controlled (decrease pit radius by using short wavelength laser or perform pit edge recording). Therefore, the development of the photon mode that takes full advantage of the properties of light) is essential for higher and larger recording density capacity.

The main purpose of this project is to investigate the feasibility of commercializing photon mode recording. Technologies that take advantage of light properties that allow ultrahigh density recording on photosensitive materials like organic photochromic or photochemical hole burning (PHB) materials that allow photon mode recording will be developed. At the same time, we must insure that materials have the appropriate sensitivity response and stability.

In the photon mode recording that employs organic molecules, a light property is recorded as an electron state by the molecule itself and conversely. Reading can be achieved if the same light property is used.

Photon mode recording not only allows high density and multiple recording, it also enables higher transfer speeds. High-speed recording of within 10^{-9} sec is possible since light reaction is completed within the lifespan of an electron excited state (psec-nsec). High resolution (recording and reading) is possible since heat dispersion and matter motion does not accompany this process. Environment friendly materials can also be selected.

3. Results

Phase One of this project which lasts four years from 1988 concentrates on identification of basic properties and research for various materials. Phase Two which lasts two years from FY 1990 studied material working and structuring technologies while Phase Three from FY 1991 compiles all these findings together. Some of the main findings are summarized below.

Photochromic material

The Research Institute for Polymers and Textiles, Matsushita Electric Industrial, Tokyo Institute of Technology, and Kyushu University are in charge of studies on photochromic material.

The Research Institute for Polymers and Textiles has developed a new memory material that combines photochromic molecules and liquid crystals. In other words, by bonding a photochromic molecule layer like azobenzene dielectric to the substrate layer, the reversible configuration of liquid crystal can be controlled by light alone and will not require an electric field. This proved to be the strong point of optical recording and optical display devices. The destructive reading of recordings and displays can be offset assuming the configuration change in liquid crystal to be a matter change during reading. Homogeneous arrangement methods were also developed for high contrast and resolution recording. Applications like high density recording on material. high-resolution display and spatially and optically modulated devices for use in parallel optical calculations, are now available.

Matsushita Electric Industrial is developing a new high density recording method that takes advantage of the photon mode recording where wavelength multiple recording using photochromic J association gives a narrow absorption spectrum. This requires many types of photochromic molecules that absorb J association over different wavelengths.

Spiropyran that absorbs over different wavelengths was newly designed with the help of molecular orbit calculations and as a result, most spirobenzopyran with Br, NO₂, and CH₃O bases were synthesized. As a result, including SP1822, BSP1822 with Br base in its indoline ring, MSP1822 with CH₃O base in its indoline ring and SP150 with sulfonyl base were proved to have superior properties. These have a total of four associations that produce sharp absorption spectra in different positions. In this manner, four-wavelength multiple optical recording was achieved. Recording energy in optical recording was also measured and in the case of SP1822LB thin film, the reduction process in absorbance by J associations was found to have a threshold value. It was also discovered that nondestructive reading is possible if a low light source is employed.

Tokyo Institute of Technology proposed the circular two-color reading method for nondestructive reading. Experiments to prove the feasibility of this method is currently in progress. In brief, photochromic dye which has a photochromic section and a two-color dye section can be used to dope liquid crystal gel with a cholesteric structure, so that the circular two-color at the dye absorption area changes with photochromic reaction.

Kyushu University aimed at clarifying molecular design policies for determining thermal irreversibility and repetition durability of photochromic molecules, by mathematical simulations and synthesis. Di-arylethene that possesses furan rings and thiophene rings can be repeatedly operated in an oxygen environment for 3.7×10^3 times and in a vacuum for 104 times. Both di-cyanoethene and maleic anhydride dielectric are not very durable while 2,3-dibenzothienyl maleic anhydride that contains benzothiophane ring exhibited high durability. These compounds are also thermally stable with a proved storage lifespan of more than 10 days at 80°C.

PHB material

The following are required before PHB material can be used as the optical recording medium:

- i) increase in write, read and storage temperature
- ii) increase in multiplicity
- iii) increase in writing speed and writing sensitivity
- iv) repetitive reading stability
- v) configuration of recording system

R&D to achieve test targets are being pursued by the Electronic Engineering Research Institute, Toray, Mitsubishi Electric, Sony, Tsukuba University, Tokyo Institute of Technology, and Osaka University.

The Electronic Engineering Research Institute aims at identifying the factors governing PHB and establishing guides for material design. Very interesting results were obtained with dye proteins like cytochrome C and myoglobin (Mb) which are PHB materials with clear cut configurations. Cytochrome C is a protein with Fe-porphine in the center which contributes to electron transmission. After substitution of the Fe in the center with hydrogen, it is dispersed in a buffer liquid glass and the resulting holes are measured. Cytochrome/glass has hole widths narrower by less than one-half when compared to those in octaethylporphine/polymethyl methacrylate (PMMA). The spread is small even when irradiation time is increased. This reflects the highly ordered three-dimensional arrangement of protein. Similar to Mb, the temperature dependency of the Debye-Waller factor (α) obtained by photon echo gives a Huang-Ryth factor (S_c) of 0.08. This is currently the smallest value and is interpreted as an extremely weak bond. At low temperatures, α is 0.92 and even at 100 K, it is merely about 0.7. This indicates that hole production is possible at high temperature of 140 K.

Toray had remarkable success in retaining holes at high temperatures and in developing "writable" materials. TCPP(Na)/PVA can be maintained at liquid nitrogen temperature for 24 hours without significant changes in its spectrum. Hole generation in this type of material is also possible even at liquid nitrogen temperature. Hole generation studies were intensified and temperature dependency of the hole width of the post-polymer in the form of deuterated PVA was measured. The hole width of porphine/polymer is believed to increase with the saturation speed of the secondary post-polymer. Holes can be made narrower by suppressing the tunneling effect of the hydrogen atoms during saturation by deuteration. Based on this concept, a system was fabricated with deuterated PVA as the post-polymer and ionized porphine TSPP(Na) as the guest molecule and the hole width measured. As expected, hole widths decreased by 30-50 percent as a result of deuteration. This system was then cooled down to liquid helium temperature and five holes were generated. Holes with a width of 2 cm^{-1} were obtained at liquid helium temperature when this system was stored for 24 hours at liquid nitrogen temperature. This proves that deuteration improves multiplicity.

Mitsubishi Electric was involved in density increment. In the DAQ/PHEMA system, hole generation was effective at wavelengths of 560-585 nm. On the other hand, holes were generated in the ABDAQ/PHEMA system from wavelengths of 580-608 nm. These two systems were fabricated into a laminated system for testing multiple hole generation. As a result, more than 600 holes were confirmed in wavelengths ranging from 565-601.5 nm. To further increase the multiplicity, multiple PHB hole generation was also tested in an electric field. Five types of lasers with wavelengths of 581.0, 581.5, 582.0, 582.5, and 583.0 nm were used to generate holes in ABDAQ/PVB under five respective electric field multiple recordings. Twenty-five holes were successfully generated. It was therefore proved that a multilayered structure and multiple electric field is effective for increasing recording density in PHB.

Sony developed a PHB recording device and studied the issues and their solutions during recording with this device. To date, Sony has shown that it is possible to generate holes in four different parts in the surface of the sample with the help of a laser beam focused to 100 μm . It also made 11 wavelength multiple recordings with 10 μm . The laser spot is now smaller and recording on a 6 μm area is possible. In this minute area, the effects of recording characteristics of the incident laser beam intensity becomes an issue if recording is to be performed in a very short time. To verify this, recording was checked by varying the laser beam intensity. Holes generated were found to be shallower if the intensity of the incident laser beam is increased for equal incident energy. It was proved that this triplet state is the bottleneck.

Tsukuba University studied the dynamics of the photon echo method for PHB. PVA and ethanol which has a similar structure was used as the matrix and their differences were noted. When HITC is used as the guest molecule, the hole width was observed to be PVA < ethanol and the nonuniform width is ethanol < PVA. The nonuniform width is wide in PVA because voids of varying sizes exist in the fractal dimension. This is understood as the hole width being more dynamically stable at high temperature for PVA matrix than ethanol matrix.

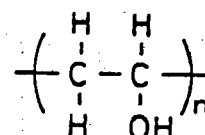
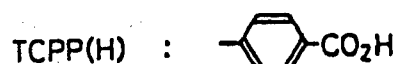
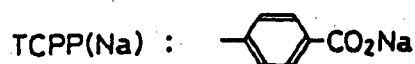
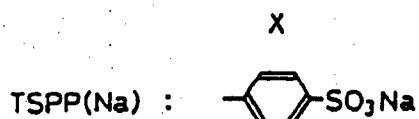
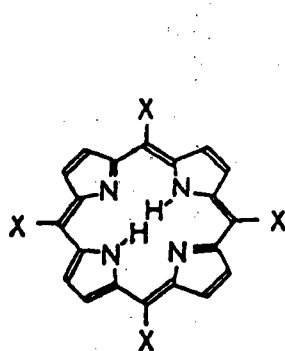
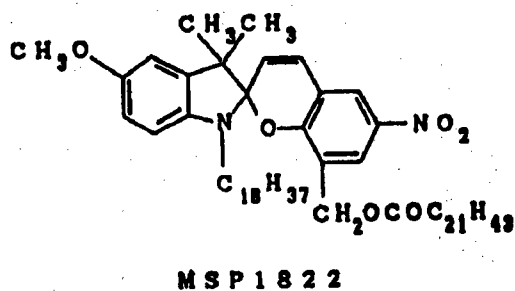
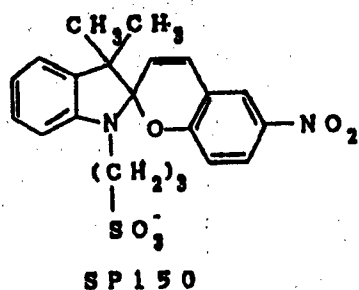
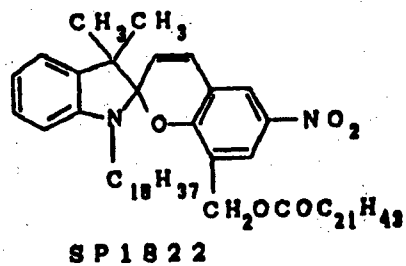
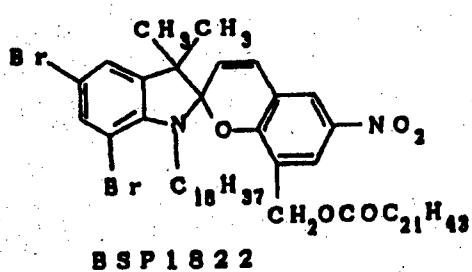
Osaka University developed the photon echo Fourier spectroscopic method for evaluating PHB materials and is currently studying the correlations between electron-lattice in a polymer. The temperature dependence of the ratio between the area of the zero phonon beam and phonon sideband to the zero phonon beam (Debye-Waller factor, α) was measured.

Material design requires a phonon sideband with high-peak frequency for maintaining holes at high temperatures. This frequency has been measured for many polymers and PVA synthesized polymer or biological polymer like dye protein is evidently an important post matrix.

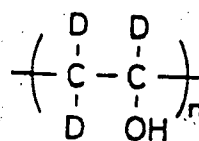
The Tokyo Institute of Technology is currently studying thermal annealing effects on optical conductivity in hydrogenated amorphous Si with PHB as the model system.

The above touches briefly on the current R&D status on photosensitive material. With the exception of some, the initial target has been achieved. The remaining issues are the increased multiplicity in photochromic material, improved sensitivity, and higher speed response in PHB material. It is hoped that solutions to these problems will be available by Phase Three of development. During the course of this project, universal principles and guidelines were developed for several new photon mode materials. Active research related to this field may also be attributed to the success of this project.

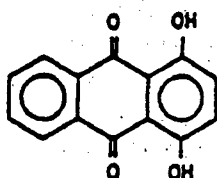
Description of codes



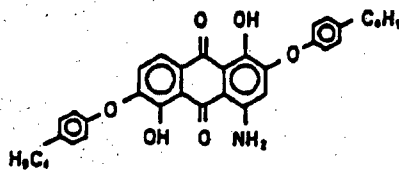
PVA



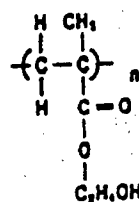
Deuterated PVA



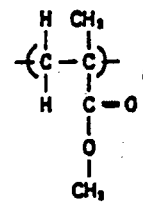
DAQ



ABDAQ



PHEMA



PMMA

R&D in Nonlinear Photon Material

926C0071I Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 61-66

[Article by Hachiro Nakanishi, professor, Tohoku University, Reaction Chemistry Laboratory]

[Text] 1. Introduction

A phenomenon is termed linear when the input and response has a straight line relationship. When the response is proportional to the input multiplied by itself once or twice, or the phenomenon is expressed as a delta function, this phenomenon is no longer a linear relationship. This is called a nonlinear relationship.

A laser beam exhibits nonlinear polarized response due to vibrating electric field. Similarly, matter that can induce various optical phenomena by varying the light attributes like wavelength, amplitude, phase, pulse width, polarization, and optical path, are termed nonlinear optical material (or nonlinear photon material in this paper).

2. Need for R&D in Nonlinear Photon Material

The age of information was heralded by developments in electronics. At the same time, an increase in the capacity of information to be handled has generated the need for higher processing speeds.

Current communications and information processing systems employ the nonlinear response by electric signals for switching, amplification, logic, and memory. All these technologies have reached their limit, particularly in their speed.

A breakthrough lies with communications and information processing techniques that take full advantage of the light properties like high speed, parallel and spatial processing, spatial bonding, and multiple high density when compared to electricity. The age of photonics is believed to arrive with the 21st century.

In photonics, the various ultrahigh-speed operation optical devices like optical switch, modulator, shutter, filter, gates, sawtooth shaped molding,

generation of ultrahigh-speed optical pulse, wavelength change, optical amplifiers, optical logic circuits and (optical memory, dynamic) and optical switch are vital.

These optical devices will not be available unless high-performance nonlinear photon devices with nonlinear response and power as weak as semiconductors are available. Existing materials cannot meet these requirements.

As a result, due to the advancement of the technologies involved and the difficulties for a single corporation (in terms of risk, capital, and time) to develop the aforementioned next-generation fundamental industrial technologies, this 10-year project was established in October 1989 to develop materials and related technologies that satisfy the device performance requirement standard (for the time being, third degree nonlinear sensitivity $\chi^{(3)} > 10^{-7}$ esu, response speed $< 10^{-12}$ sec, absorption coefficient $< 10^2 \text{cm}^{-3}$). This project will not handle second-degree nonlinear optical materials like wavelength modulation devices or electrooptic modulation devices that have short term results. Longer term issues like third-degree nonlinear optical materials will be dealt with.

3. Overview of R&D

It is made of the four following sections:

(1) Identification Mechanism for Nonlinear Optical Phenomenon

Clarify the identification mechanism for nonlinear optical phenomena like wavelength modulation, refractive index change, absorption coefficient change, and dielectric dispersion. At the same time, explain the relationship between the time characteristics of high-response speed/saturation phenomenon and material performance. Search for new nonlinear optical phenomenon and compile the findings into a design guide for high-performance nonlinear material.

(2) Material Development

Organic: By using molecule design with attention paid to atom and molecule arrangement, search for organic materials with low and high molecular weight which exhibit high nonlinearity and response speed. Develop synthesis technology.

Dispersed: Using ultrafine grains like structure controlled organic molecules and semiconductors, as "guest," search for dispersed type manufacture with organic or glass dispersed within the matrix and with high nonlinearity and response speed. develop adjustment (design, synthesis) techniques.

(3) Development of Material Fabrication Techniques

Crystal growth: Develop techniques for growing organic crystals of a size, perfectness, and configuration that can sufficiently express the crystal's nonlinearity.

Dispersion: Develop techniques for homogeneously dispersing high concentrations of ultrafine structure controlled particles within the matrix material.

Superlattice: Develop techniques for fabricating two- or three-dimensional superlattices from multiple numbers of atoms and/or molecules.

(4) Development of Evaluation Techniques/Material Evaluation

Develop ways to evaluate the structure of nonlinear photon materials, ways to evaluate and measure nonlinear optical constants, and optical response constants.

4. Development Status and Results

Nine corporations including one foreign, five national research institutes and three universities took a full two years to achieve the following status in the above-mentioned four development themes:

(1) Clarification of Identification Mechanism for Nonlinear Optical Phenomenon

- **Molecule design:** Various methods like PPP, ab initio, MP2 and CNDO were studied for determining properties of third-degree nonlinear optical molecules (molecule super polarizability, γ) from quantum chemical calculations. As a result, data that matches measured values of γ was obtained in a short time by the semi-experience molecular orbit (PPP-SDCI) method. This can be used as a molecular design tool at the material search level. This method indicates the previously difficult to predict relationship between conjugation length and γ . These are results that will be beneficial to future developments.

- **Appearance mechanism:** The extremely large nonlinear response by aggregates of pseudo isocyanine (PCI) (J-association groups) shown by the sharp peak in the absorption bandwidth, is displayed by the absorption saturation method using nanosecond pulse. First, the nonlinear refractive index is determined from experimental results. This value is then adjusted as a third-degree nonlinear optical characteristic (nonlinear susceptibility, $X^{(3)}$) to become 6×10^{-5} esu. When determined by the degenerative four wavelengths method (DFWM), $X^{(3)}$ becomes 4×10^{-7} esu. Both values meet the device specifications. The difference in the values may probably be due to the appearance of the nonlinear response and may be promising in future developments and for determining response speeds.

- **Function search:** The possibility of a pulse compression within a femtosecond resonator for an impact type pulse mode synchronized laser was studied using organic crystal thin films or organic molecule dispersed polymer thin film. As a result, pulse compression was first made possible by trapping organic molecule systems with large nonlinear optical characteristics within the resonator.

(2) Search for Materials and (3) Material Fabrication Techniques

(Organic Systems)

- **Low molecular weight:** Chiral nonlinear optical materials with optical Kerr shutter operated by self-polarized rotation or unidirectional plane polarization that is strongly dependent on the light intensity, were proposed. Various helical insulators were synthesized and after measurements made on the hexahelical insulators, a very weak signal resulting from the nonlinearity in chiral was observed. This is a result that will help pioneer new frontiers in the search for new materials.

- **Polymer crystals:** Repeated efforts were made in design and synthesis of the most popular and widely employed conjugated polymer system called polydiacetylene for increasing electron density. A material with nonlinear susceptibility was developed to meet device specifications and functions that are better than existing ones by an order of magnitude (about 10^{-3} esu by the third harmonics generation method (THG) during resonance). As a result, other countries have begun studies on the same material. At the same time, these provided new hints for synthesis of conjugated polymers with larger susceptibilities. Future important developments like the increase of susceptibility through intermolecular interaction even for the same type of molecule will be possible in dye thin films which are employed as model matter.

- **Polymer thin film:** Possibilities for fabricating thin films were ascertained by determining the feasibility of new synthesizing conjugated polymers with electron acceptance and donation bases. At the same time, a measuring device to evaluate the susceptibility by changing the wavelength was fabricated and its effectiveness proved for screening the various polymer synthesis stages. It will be a promising appliance for evaluating new materials.

- **Crystal growth:** The degree of vacuum required for growing an epitaxial thin film by vacuum vapor deposition is high. A device that can control temperatures ranging around room temperature was fabricated. Thin films grown at ultraslow speeds was observed to have surface areas of more than 10 times that grown by existing vacuum vapor deposition methods. Crystals were also found to have fewer defects. Results indicate that molecular alignment control will be possible in the future.

(Dispersed Systems)

- **Homologous CuCl:** Studies on thermal treatment conditions for fused deposition of CuCl enabled particles with a small radius spread to be available; the $X^{(3)}$ in glass with minute particles of about 80 Å dispersed in it was observed to be 7×10^{-6} esu by DFWM. Fabrication of dispersed glass by applying the infiltration or sputtering method on porous glass was studied. Fabrication of glass thin film with minute particle concentration of more than 10 times that when using the fused deposition method became possible. Test fabrications of particle dispersed glass were also studied on CuBr and CuO₂ and preliminary evaluations have shown values to be equivalent to that of CuCl.

- **Homologous CdS:** P_2O_5 glass was selected as a glass with high solubility in semiconductor compounds, low melting point and thermally stable. Concentrations of particle dispersion of CdSe and CdTe in the glass were found to be more than 50 times higher than conventional semiconductor doped glass. The former was confirmed to be more than 5×10^{-7} esu when measured by DFWM at room temperature while the latter was an order of 10^{-7} esu. Molding of the glass that contains high concentrations of dissolved semiconductor by ultrarapid cooling in the double roller method without crystal deposition was tested. Thin films of several tens μm were achieved.

- **Material synthesis:** A device based on the new concept of using high energy pulse laser was developed as a means of fabricating semiconductor ultrafine particles. As a result, ultrafine particles of about 4-10 nm of GaAs, CdS, and CdTe were fabricated. This will be a promising development in the future.

- **Organic dispersion:** CdS ultrafine particle dispersed polymer film was successfully fabricated by the organosol method. A method to control particle size using the catalytic reactions induced by light absorption by semiconductor ultrafine particles was proposed and its feasibility proved. This method can be applied to various superconducting ultrafine particles and future developments look promising.

(Superlattice)

- **Organic base:** The relatively unknown superlattices should be fabricated from organic molecules. A molecular beam epitaxy (MBE) device equipped with various analytical instruments was created to achieve the maximum degree of vacuum required at this point of state-of-the-art. Experiments on growth of single molecule layer have already begun. A test device to analyze laminated structures of organic superlattices and their time response characteristics, was also fabricated. Calculations on supermolecules by the nonexperience molecular orbital method was attempted for the first time to improve their nonlinear optical characteristics during superlattice fabrication. Increase in size of the constant was confirmed and future developments look promising.

- **Semiconductor base:** Matrix glass which is an important component material in superlattices and having a low melting point and low coefficient of expansion was developed. Even in the case when CdS dispersed glass thin film was fabricated by the alternate multielement sputter and vapor deposition method, effective quantum size was confirmed. Experiments were conducted on fabrication of Zn_xCCd_{1-x} base II-VI group semiconductor compound superlattice thin films. Various test samples with differing thicknesses of the quantum well layer were fabricated. Particle confinement within the well layer was confirmed.

(4) Development of Evaluation Techniques/Material Evaluation

- **Common evaluation:** The phase conjugated DFWM optical system was designed as a common measuring device for screening synthesized materials. Evaluations were made on the ultrapolarizability and susceptibility of various materials

like vitamin B₁₂, thiaheteroherisen [phonetic], CdS or materials with dispersion of ultrafine metallic particles. Useful observations were reflected in material design. A common evaluation device for response speed is being constructed.

- **Reliability evaluation:** The THG method that is most popularly employed for measuring susceptibility has identified various measuring conditions to obtain data of high reliability. Glass with a very-high refractive index and $X^{(3)}$ value and not silica glass was confirmed to be a better standard.

- **Structure evaluation:** Highly analytical solid nuclear magnetic resonator (NMR) and electron spin resonance (ESR) methods were employed to determine the structures of insoluble and infusible nonlinear optical materials. Key results in the search for organic materials were obtained.

- **General Study 1:** The relationship between the exciton ultra emission mechanism in CdS ultrafine particle and lattice vibration was first discovered while studying energy saturation in various materials under the optically pumped state. The real and conjugate part of the susceptibility was simultaneously measured by using the femtosecond pulse in the Mach-Zehnder interferometer. A method to measure the time response for both parts was also proposed.

- **General Study 2:** Organic crystal growth for applications in feasible optical devices like channel guides or core fiber were studied and at the same time, a device concept that allows thermal effects to be ignored was proposed.

- **General Study 3:** Basic information on semiconductor ultrafine particle dispersed glass was evaluated from its quantum size and at the same time, determination of the electron level and evaluation of the lifespan was made by picosecond stroboscopic analytical measurements.

5. Future Developments

Only typical successes and overviews have been described here together with advances made. Although only two years have elapsed after commencement of the project, all results were confirmed to be world standard or even lead others. Issues were many. There is very keen competition in this field particularly since progress is made at an amazingly fast pace. Shortly after proposals on the theories for high-performance materials, device concepts, and an understanding of the problems involved, research was announced one after another. This project leads the rest of the world. Not only the common evaluation system but also the proposals for test samples and potentials were all conducted on a cooperative basis with international and domestic members from the industrial, academic and government sectors. Those interested in detailed results of this R&D project can refer to the first and second optoelectronic material symposium drafts (editing, publishing: Japan High Polymer Center). Those interested in everything about this field can make inquiries as there has been much material prepared on them.

Technical Development Trends in Fine Ceramics

926C0071J Tokyo SEKAI NI HABATAKU JISEDAL PUROJEKUTO in Japanese 19 Feb 92
pp 69-74

[Article by Shinroku Saito, Kanagawa Science Technology Academy]

[Text] The general study group for fine ceramics of the Jisedai Project had its 4th meeting at the end of last year. Powder production, molding, sintering, bonding, finishing, strength tests, NDT, triology, and various kinds of environmental tests were done. Various quality and verification tests were conducted on testpieces like still and movable blade models. The results of such research efforts and issues forecast in the product development in the near future will be described in this symposium.

Advanced technology field	Electronics (Hardware (ME, opto-electronics), information processing, communications (network))	Biotechnology (Physiology activating peptide, monoclonal antibodies, immobilized enzyme, microorganisms, etc.)	New materials (Structural materials, functional materials)	New energy (Solar batteries, fuel batteries, fuel breeder, coal liquefaction, etc.)
(1) Dimension of impact ① Product--appearance of new product ② Changes in production process for existing products				
(2) Industry ① Changes in industrial structure ② New business sector				
(3) Society ① Daily life ② Social system * Citizens' awareness				

Survey by Japan Development Bank/
222

(Note) ————— Now ~ 1990
----- 1990 ~ 2000

Figure 1. Degree of Impact by Advanced Technology

Figures 1 and 2 show the developments we have achieved. It is difficult to explain the development of new materials including ceramics in 1990 without touching on electronic parts. Figure 2 shows that many products have already

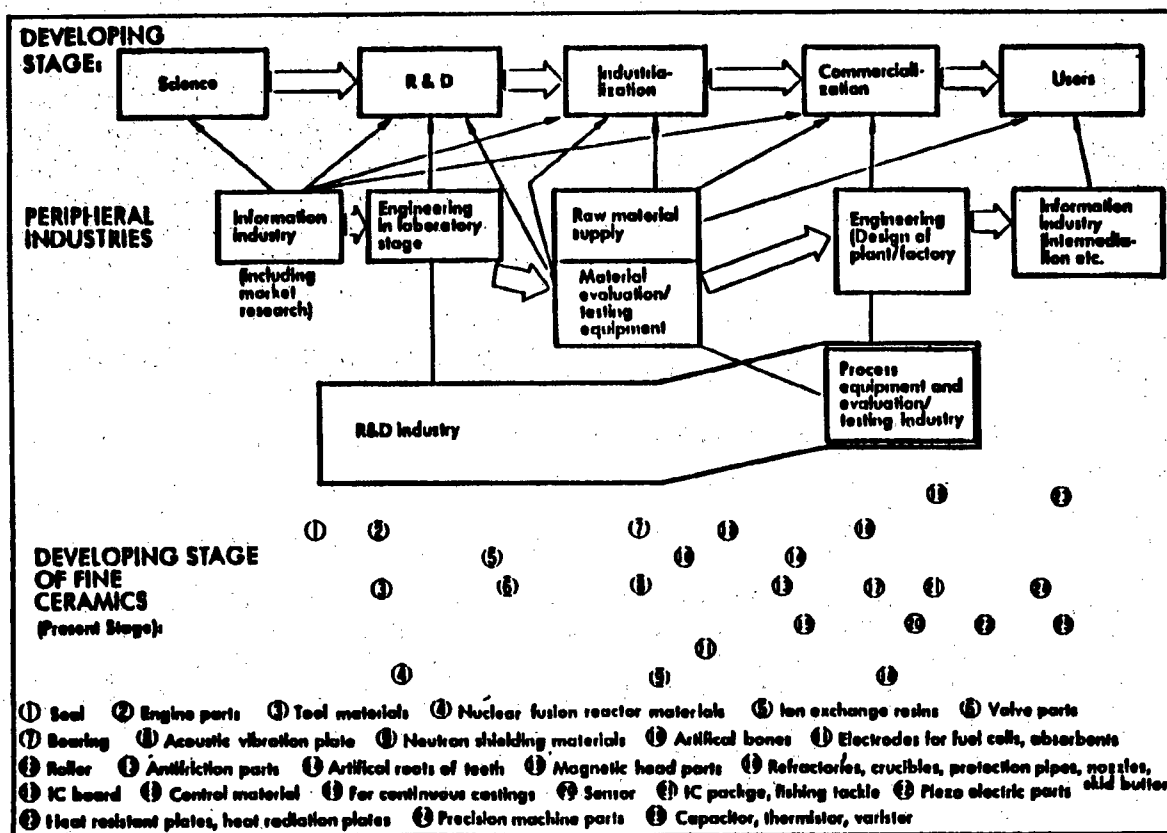


Figure 2. Developing Stage of Fine Ceramics

Source: Industrial Research Division, the Long-Term Credit Bank of Japan, Ltd.

been marketed. Based on this, Figures 3 and 4 show that there is a significantly high number of chemical abstracts.

Let us trace the production process for ceramics. First, the powder must be selected and Figure 5 illustrates only those methods for fabricating inorganic and metallic thin films which can also be employed in fabrication of ultrafine powders. Figure 6 is an example of the alkoxide method while Figure 7 shows a vibration mill. Figure 8 is a real example of a very finely crushed ball or submicron particles produced by conventional methods. Figure 9 is an example where a thin film is made from these ultrafine particles. Figures 10 through 13 show the host guest method where various intercalation characteristics are displayed. The host in Figure 13 in particular uses organic polymer Langmuir-Blodgett (LB) thin films. The creation of this multilayered two-dimensionally controlled silica at room temperature is epochal. Bonding in the c-axis did not occur until about 600°C. These methods are suitable for obtaining superior nanocomposite configurations; however, at high temperatures, it becomes difficult to avoid grain cross. In other words, nanocomposites limit themselves by the conditions under which they are applied.

CHEM. ABSTRACTS TOTALS

ZIRCONIA
ZEOLITE
SILICON
NITRIDE
CEMENT
SOL GEL

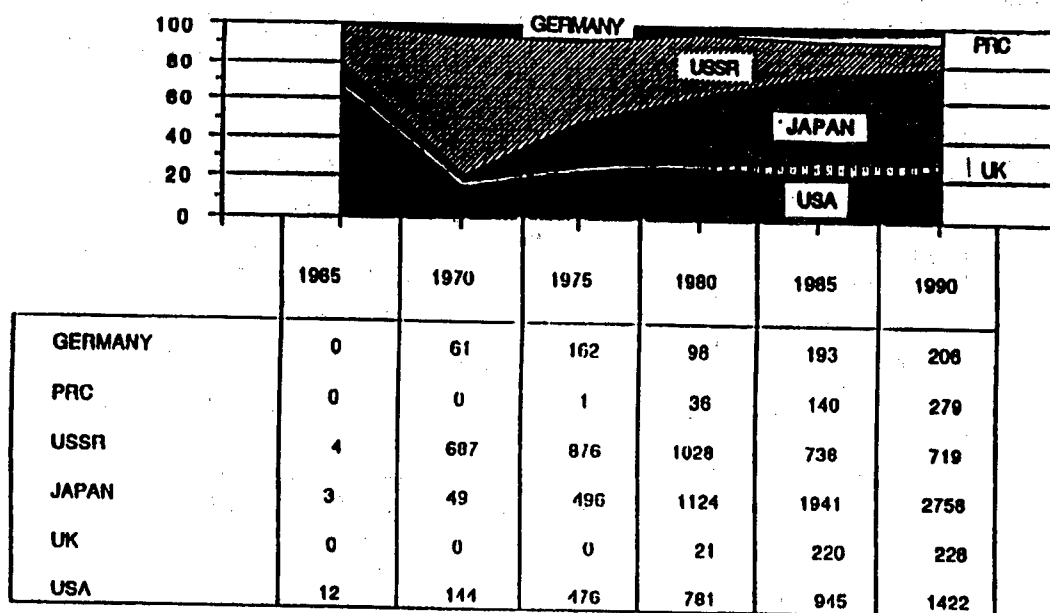
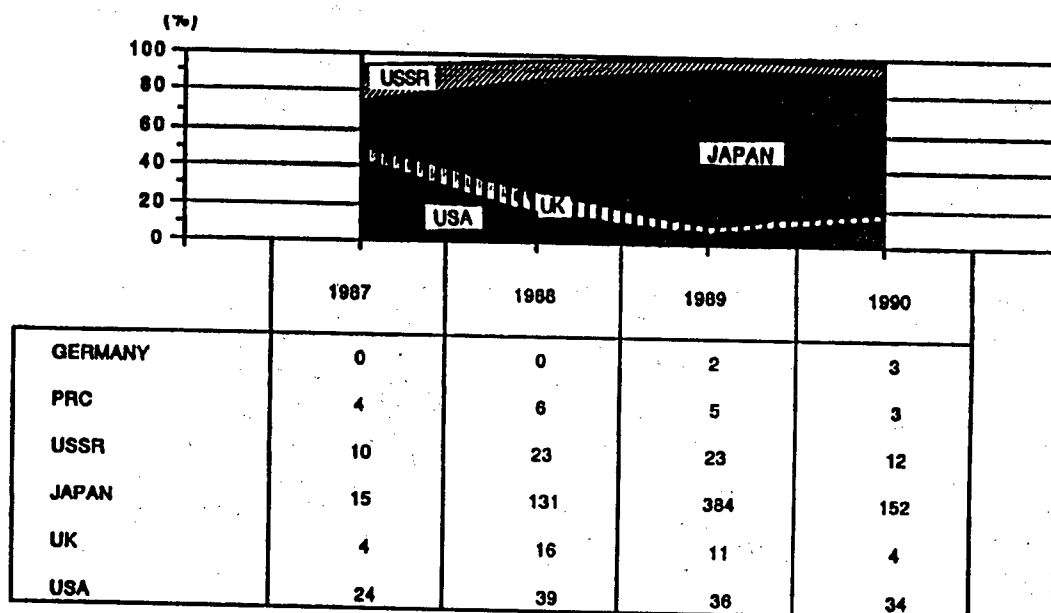


Figure 3. 'Market Share' of Ceramic Research



PUBLICATION YEAR
Figure 4. Ceramic Superconductors

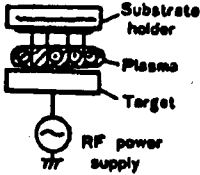
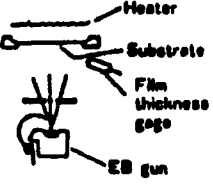
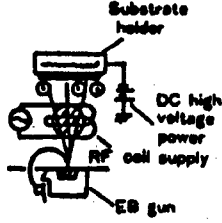
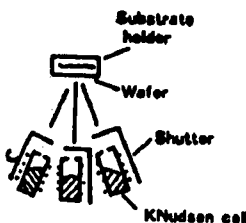
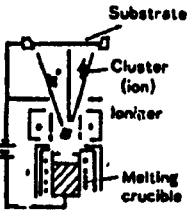
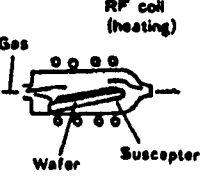
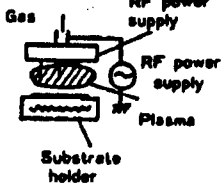
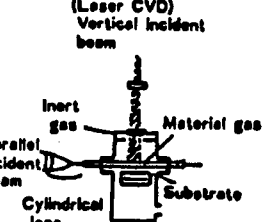
Method	Sputtering	Vapor deposition	Ion plating	MBE
Principle				
Method	ICB	CVD method	Plasma CVD	Optical CVD
Principle				

Figure 5. Outline of Thin Film Preparation

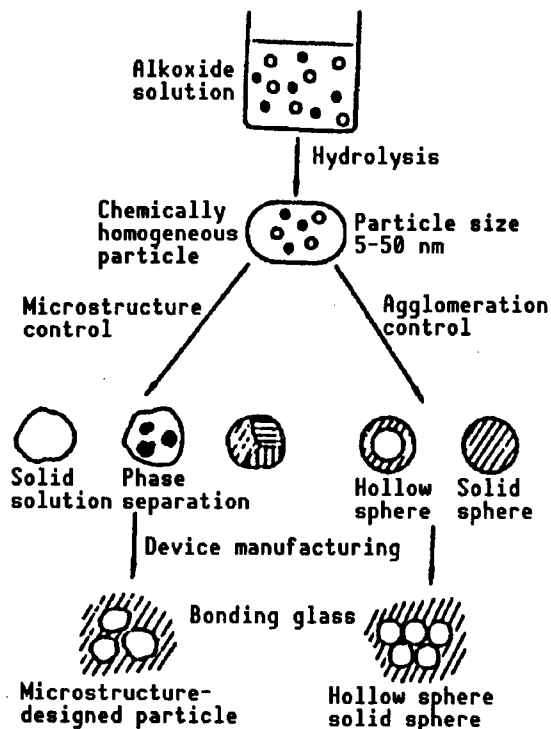


Figure 6. Micro and Macrostructure Design of Powder Particle and Agglomeration by Metal Alkoxide

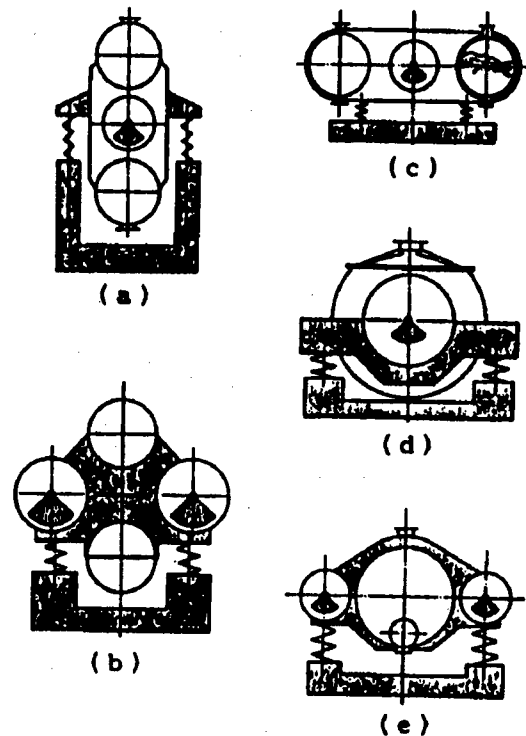
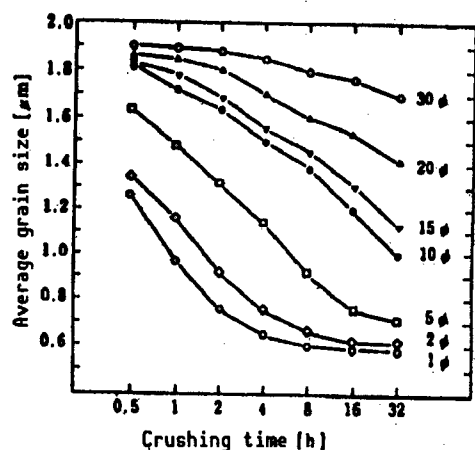


Figure 7. Vibration Mill With Circular Vibration



Prepared by Kenji Tanaka, Kikuo Wakino
Murata Seisabusho

Figure 8. Crushing Time Vs. Average Grain Size When BaTiO_3 Is Ground in Vibration Ball Mill

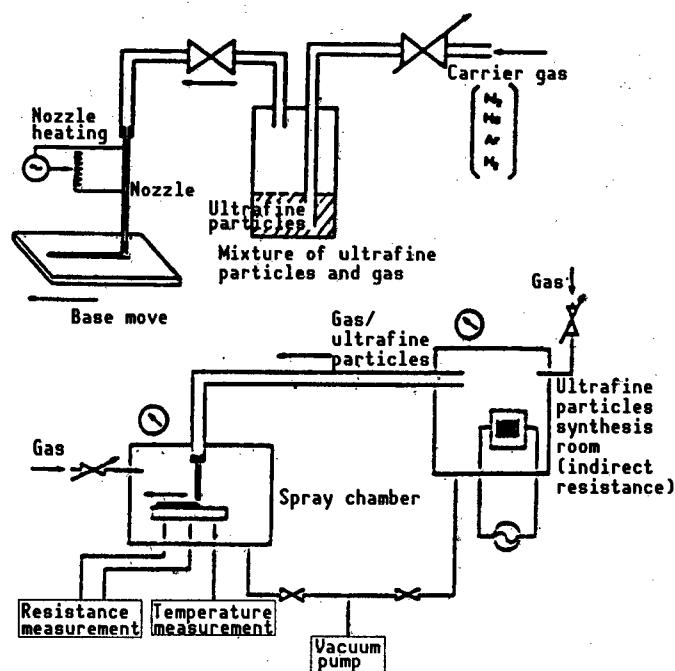


Figure 9. Gas Deposition Method Using Ultrafine Grains

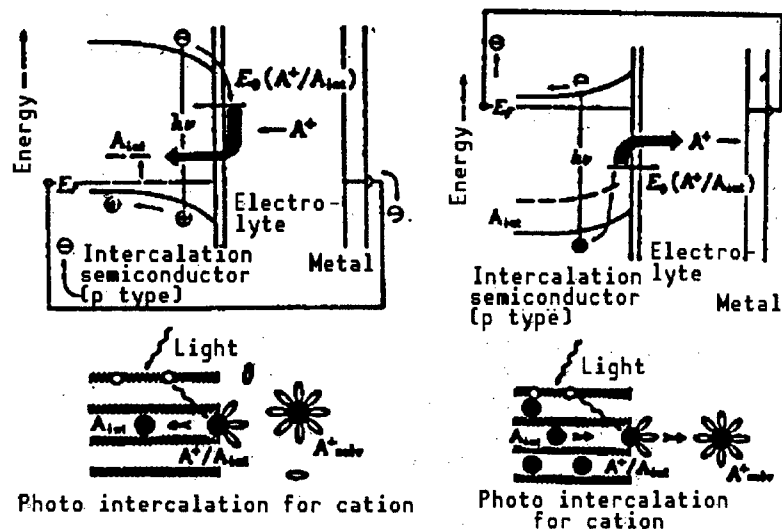
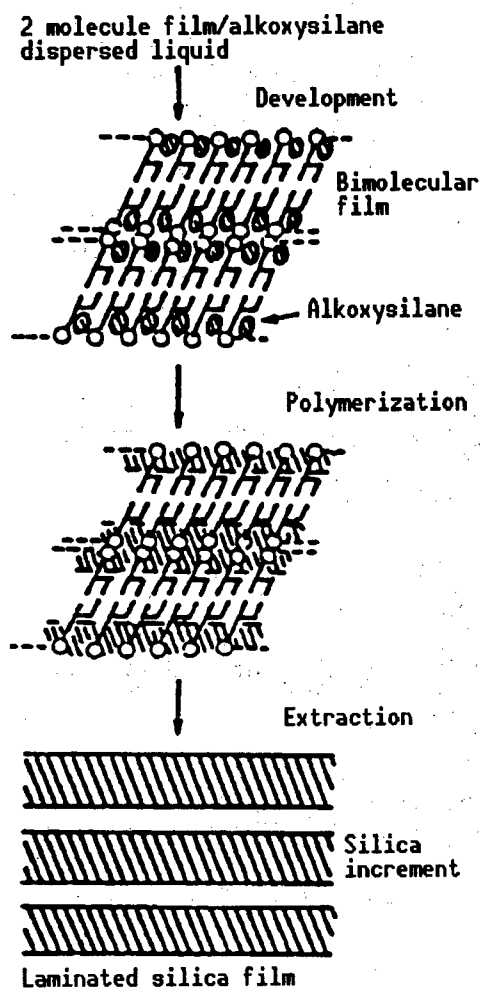


Figure 10. Principle of Photo Interpolation in p- and n- Type Semiconductors



Prepared by Kanji Sakata, Chemical Structure Project, the Research Development Corp. of Japan and Toyoyoshi Kunitake, Kyushu University

Figure 13. Block Diagram for Ultrathin Silica Film Fabrication Methods

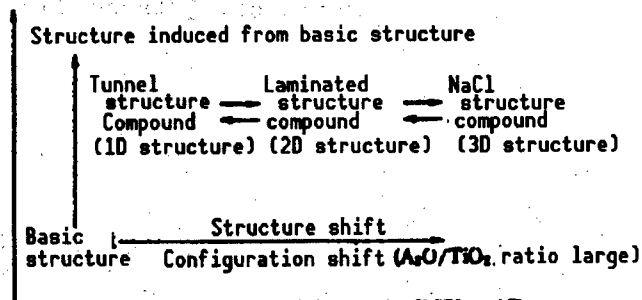


Figure 11. Regularity of Configuration and Structure of Titanium Oxide Alkali, Metal, Compound Groups

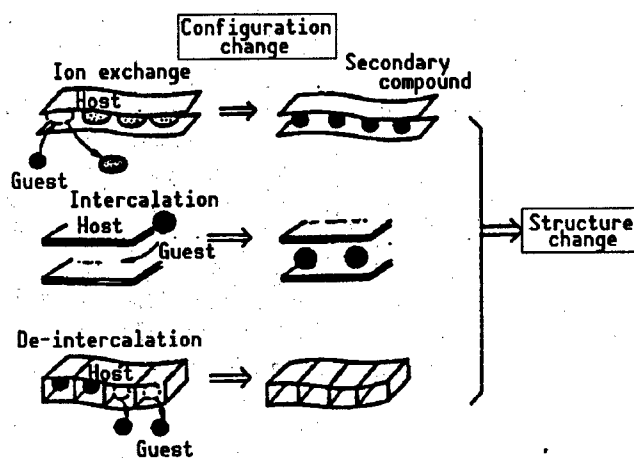


Figure (?). Host-Guest Reaction Application and Configuration Change

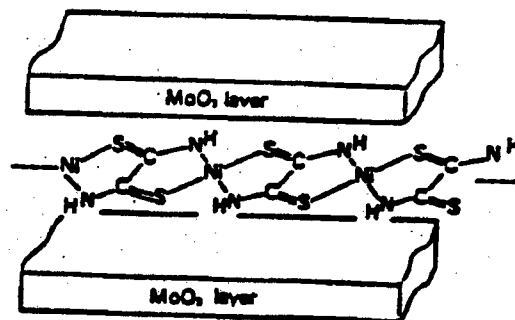


Figure 12. Schematic Structural Models of Coordination Polymer

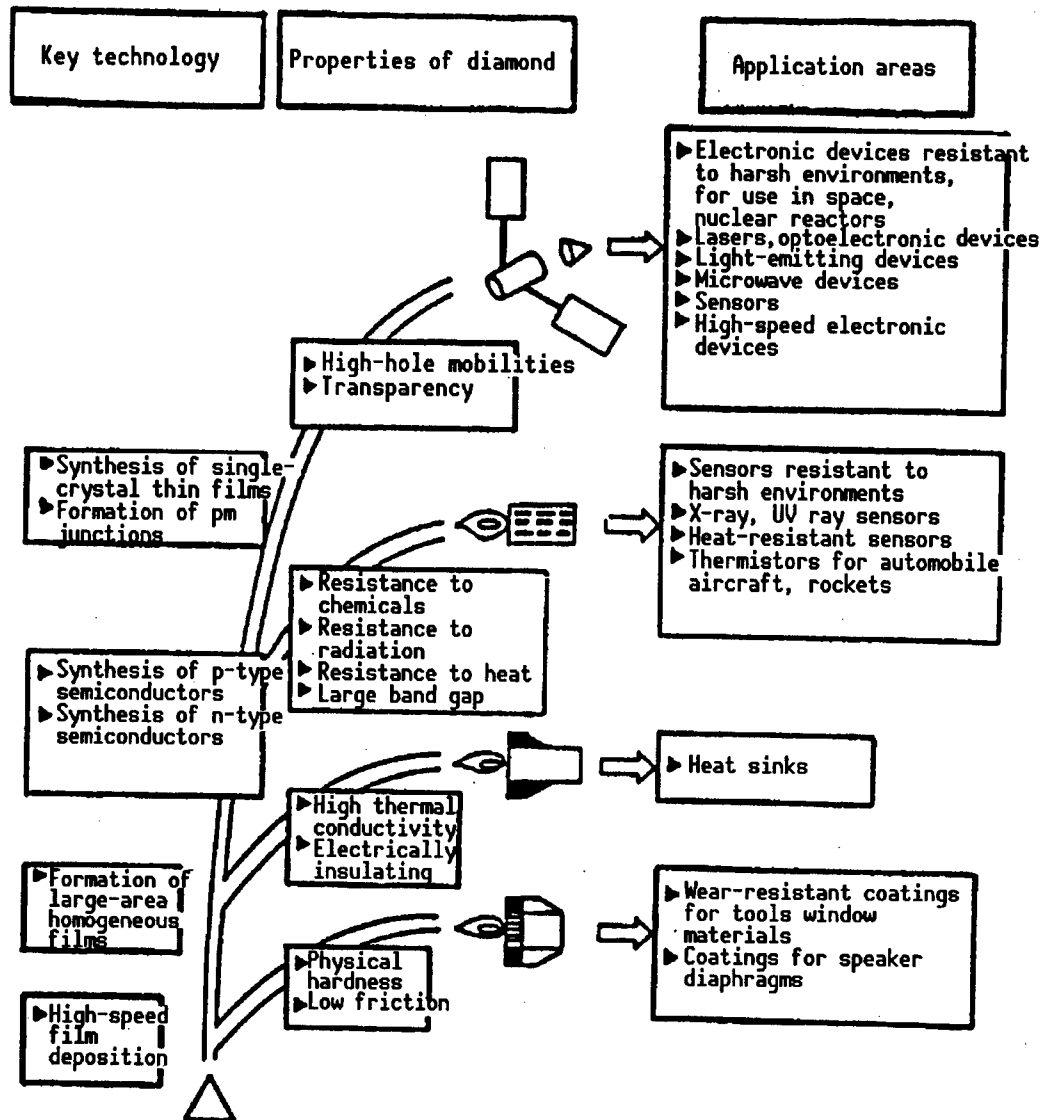


Figure 14. Vapor Phase Synthesis of Diamond Thin Film and Its Applications

Figure 14 is the newly focused gaseous diamond constituent and development of a diverse type of applications. Besides applications in automobile car parts like surface-coated abrasive-resistant machine parts, there are also potential applications like high temperature np junctions. Figure 15 shows a composite material fabrication method called rheo process that does not depend on conventional annealing methods. Figure 16 [not reproduced] shows the microstructure of a cross section of the test sample. This is suitable for conjugation and mass production when the specific mass difference is large. Vacuum sintering, high pressure sintering and bonding are not shown in the diagrams but their application in the marketing of functionally gradient material (FGM), smart material, and intelligent materials are gathering much attention. The breakthrough in LB thin films is the shift in focus on

deposition of solid material from their gaseous or liquid phases to that by biodeposition. The bio-generation mechanism for pearls, bones, and gallstones will be a new starting point in science. (30 January 1992)

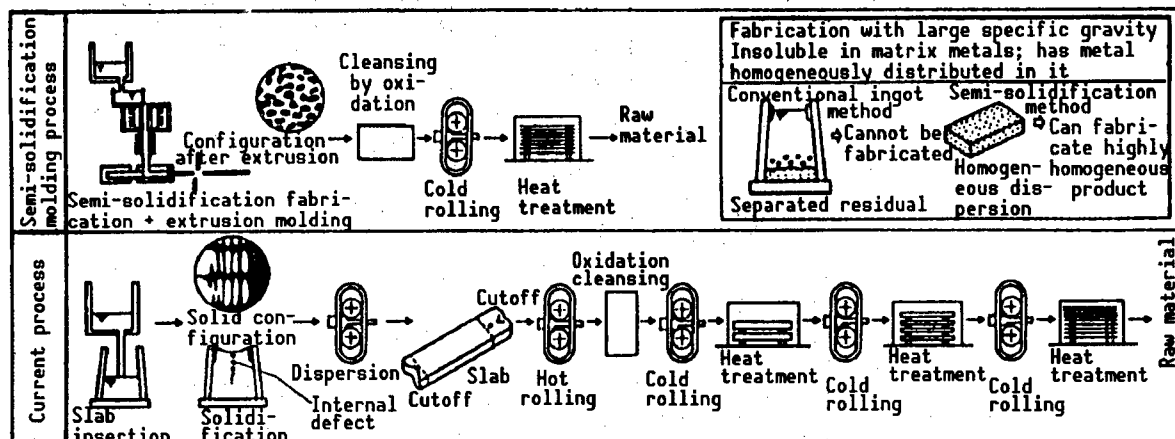


Figure 15. Comparison Between Semi-Solidification Molding Process and Current Process

R&D of Fine Ceramics

926C0071K Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 75-81

[Article by Hideyo Tabata, director, Ceramics Fundamental Department,
Government Industrial Research Institute, Nagoya]

[Text] 1. Introduction

Ceramics have been used on an experimental basis in structural materials for machine parts since the 1950s because of its heat resistance, corrosion resistance, high strength, and abrasion resistance but not much progress was made on the material because of its brittleness and diversity in these characteristics. The brittle material project (BMT) was established in the early 1970s after ceramics was proposed as a replacement material for heat-resistant alloys in some parts of high-performance engines developed in the United States. This national project used ceramics as a structural material. World interest in energy conservation increased after the two oil crises in the 1970s, and to improve operative effectiveness of heat machines that burn oil, created a demand for engines that can be operated at higher temperatures. This prompted the United States and Germany to begin successive national projects on ceramic gas turbines. Japan too brought up "R&D in Fine Ceramics" as part of the Jisedai Project begun in 1981. This project did not target development of specific equipment or systems like in other projects (Large-Scale Project, Sunshine Project, Moonlight Project, etc.) but instead targeted the development of basic ceramics manufacturing, evaluation, and application technologies.

The ceramics employed are silicon nitride and silicon carbide which are expected to have high strengths at particularly high temperatures. The main objective is the realization of high-strength characteristics and reliability that did not exist before.

"Fine ceramics" began, like other projects, as a 10-year project. Phase One was FY 1981-83, the second was FY 1984-87, and Phase Three was from FY 1988-90. New research themes were added after it changed to "Development of Factor Technologies for Coal Gas Ceramic Turbines" when a special budget was introduced in 1986 for the development and promotion of electric power supplies. As a result of extending the R&D period for two more years, the

whole project will last a total of 12 years and therefore 1992 will be the final fiscal year.

An overview of the results achieved in R&D in the 10-year Fine Ceramics Project will be described in this paper.

2. Development Target and Results of Phases One and Two

2.1 Manufacturing Technology

2.1.1 Synthesis of raw materials

Since the silicon nitride and silicon carbide powdered raw materials used for making fine ceramics depended largely on imports at the time when the Jisedai Project was implemented, a major proposition was to produce these materials domestically such that their properties meet world standards. Target performances for the powdered raw materials are listed in Table 1 with special reference to those properties that were considered superior on a world level at that time. R&D commenced with work on several manufacturing techniques being done at the same time. The results of Phase One are listed under "Achieved Value" and it was observed that powdered raw materials that satisfy the targeted performance can be synthesized regardless of the manufacturing method.

Table 1. Target and Achieved Values for Properties of Powdered Raw Materials

Material	Production process	Powder density (g/cm ³)	Specific surface area (m ² /g)	Average particle size (μm)	α phase percentage (%)	Purity*	Metal impurity				Total oxygen weight (%)
							Total weight	Fe	Ca	Al	
Silicon nitride	Silica reduction method	>3.11	>6	≤0.8	>96	>97.5	<500	<100	<100	<100	---
		3.136	6.85	1.07	97.8	98.47	123	54	3	15	0.82
	Metallic Si nitridification method	>3.11	>20	≤0.5	>90	>97.5	<750	<120	<100	<300	---
		3.12	20.7	0.50	93.1	98.3	283	31	14	144	1.20
	Vapor-phase synthesis method	>3.10	>6	≤0.9	>90	>98	<300	<30	<20	<100	---
		3.19	7.0	0.65	95.4	99.3	34	<1	5	0.42	0.42
Silicon carbide	Solid-phase synthesis method	>3.10	>15	≤0.6	---	>96	<300	<50	<70	<20	<0.5
		3.189	14.9	0.71	---	98.72	236	48	2	17	0.59

*Purity definition
SiN: 100 - (Total metal impurity + Si in free silica + free Si + C + O + C I)
SiC: 100 - (Total metal impurity + free silica + free Si + free C)

Phase Two made detailed studies on the effects of changes in the mass production and economic manufacturing process on product quality.

2.1.2 Molding and sintering techniques

The relationship between the properties of the powdered raw materials and the various manufacturing processes and the final product must be clearly understood before reliable manufacturing techniques for nonoxide ceramics like silicon nitride can be established. Therefore, establishment of process techniques that allow manufacturing of high-performance materials with

superior reproductivity were targeted. These materials were classified into three types—materials with high strength, corrosion resistance, and high-precision abrasion resistance—depending on their application environment based on their future potential applications. These materials were then treated for a fixed number of hours (1,000 hours) at a predetermined temperature and then tested for the strength and reliability (Weibull factor) specified at the temperature shown in Table 2.

Table 2. Target Performance Values and Achieved Values in Phase One for Each Material

	High-strength material		High corrosion-resistant material		High-precision abrasion-resistant material	
	Silicon nitride	Silicon nitride	Silicon nitride	Silicon nitride	Silicon nitride	Silicon nitride
Ambient temperature	1200°C		1300°C		800°C	
Strength (average tensile strength)* (kgf/mm ²)	>30		>20		>50	
	55.9	39.5	48.4	32.6	67.0	59.1
Reliability (Weibull coefficient)*	>20		>20		>22	
	32.9	20.3	23	18.6	17.4	19.4
Characteristics	Durability (creep strength)** (kgf/mm ²)		Corrosion resistance (increased oxidation) (mg/cm ²)		Abrasion resistance (specific abrasion loss) (mm ³ /kgf·mm)	
					<10 ⁻⁸	
	>10	>15	<1		7.5x10 ⁻⁸	6.0x10 ⁻¹⁰
					Precision (degree of surface smoothness) Rmax(μm)	
	Did not fracture	Did not fracture	0.32	1.0±0.1	<2	
					0.8	0.51

Upper values: target performance, Lower values: achieved values

* Performance after being maintained in atm for 1,000 hrs at above ambient temperature

**Did not fracture after being maintained in atm for 1,000 hrs at above ambient temperature

Note: Performance at normal temperature

The shape of the test sample satisfied all the characteristics targeted in Phase One, as is shown in Table 2.

In Phase Two, a testpiece with target strength, corrosion resistance, and abrasion resistance was fabricated. A piece of this test sample was cut off and studied to see if it satisfied the performance targeted in Phase One. It was confirmed that the strength characteristics in all materials satisfied those targeted except for the Weibull factor for strength in silicon carbide material. This was probably due to the difficulty of uniformly molding and sintering parts.

2.1.3 Molding and bonding techniques

Molding techniques were partially studied from the last fiscal year of Phase One and full-scale research was done upon entry into Phase Two. Emphasis was placed on the development of very precise molding devices or complex molding techniques that are particularly speedy, precise, low-energy consuming, and economical. The successfully developed highly rigid and precise grinding and molding device has a grinding performance and ratios that meet world standards.

In Phase Two, interceramics and ceramics-metal bonding techniques were developed using silicon nitride and silica parts with simple configurations. Satisfactory results were achieved for interceramics bonding with any material. Techniques to bond ceramics to metals and alloys were studied for neutralizing the resulting thermal stress.

2.2 Evaluation Techniques for Characteristics

2.2.1 Evaluation of characteristics

In Phase One, synthesizing techniques for powdered raw materials were emphasized. At the same time, the suitability of the evaluation techniques for the properties of the powder was studied. Also, the correlation between the various properties of the powdered raw material and those of the sintered sample was ascertained.

National research bodies concentrated on the evaluation methods for strength, abrasion resistance, and corrosion resistance of the sintered sample. The consortium concentrated on the development of a test device for evaluating various properties of the sample; it also tried to establish models for the evaluation techniques. These results were employed in the measurement and evaluation of the properties of the various materials, in Phase One and the last fiscal year of Phase Two.

2.2.2 Nondestructive testing methods

Studies were made to understand the status of nondestructive testing methods. A detailed review of these methods, including previous relatively unreported, photoacoustic spectroscopy (PAS) was applied for studying surface defects while the X-ray CT scan method was applied to internal defects.

2.3 Application Techniques

Design and model evaluation techniques for applications began in the last fiscal year of Phase One. In particular, test methods for very strong, corrosion-resistant and precise/abrasion-resistant models fabricated by molding and sintering techniques developed during Phase Two were checked. Test devices were developed. In the final fiscal year of Phase Two, characteristics of model parts were evaluated with the help of high-temperature rotating tests, heat impact tests, and air bearing tests. At that time, it was proved that world standard materials were developed.

3. Development Target and Results of Third Phase

Phase Three began in 1988 and target performance values for large complex shaped model parts in ceramic turbines for coal gasification was achieved. R&D on model design, test evaluation, material design, molding, and sintering as well as molding, welding, and quality assurance tests were performed as part of the "Turbine Parts Technical Development" project. Parallel to this, new "material technology development" items were identified to develop advanced ceramics materials. As a result, toughened and surface strengthened materials were developed.

National research institutes clarified destruction mechanisms under the "Destructive Strengths at High Temperatures" project while under the "Manufacturing Process Technologies" project, process technique evaluation, mechanical molding techniques, toughening techniques, and surface strengthening techniques were developed. Under the "Product Properties Evaluation" project, evaluation techniques for the strength, abrasion resistance, corrosion resistance to high temperature gas and roughness of the sintered sample were studied.

3.1 Development of Element Technologies for Turbine Parts

Secondary and allomorph models of still and movable wings in the gas turbine were created as a result of a combination of the raw material synthesis techniques, fabrication process techniques, and molding/bonding techniques developed during Phase Two in Phase Three. The aim was to achieve a series of techniques ranging from design, molding/sintering to processing/bonding. The movable wings are basically made of silicon nitride while still wings are of silicon carbide. The various values targeted by these respective materials are listed in Table 3.

First, a secondary and allomorph model for the part element (still and movable wing) in the ceramics turbine for coal gasification in the "Model Design/Test/Evaluation" project. Strength tests were conducted on the respective models for the design and fabrication of a strength evaluation device that can perform high-temperature rotating tests on the movable wing model and heat impact tests on the still wing model.

Secondary and allomorph models of the movable wing made of silicon nitride and the still wing made of silicon carbide were fabricated for checking "material design" and "molding/sintering" techniques. Rotating destruction tests and heat impact destruction tests were performed while at the same time, the cutoff sample from the model was tested for strength and toughness against destruction. Targeted results were achieved. However, with the exception of some silicon carbide, the tensile creep under a particular stress could not exceed 10,000 hours. This delayed destruction property continues to exist in our attempt to achieve the targeted performance in the still and movable wing that is being developed under the generalized technology implemented in FY 1991-92.

The targeted values in Table 3, with the exception of a few, were achieved in the "molding/bonding" technology.

Table 3. Target Performance for Development of Turbine Parts Factor Technologies

	Silicon nitride	Silicon carbide
Material design and molding, sintering	<p>Modified model for mobile blades, secondary model for rotative destruction tests, strength verification for cutoff test samples</p> <ul style="list-style-type: none"> • Instant destruction ≥ 600 MPa (1,250°C) • Delayed destruction ≥ 250 MPa (10,000 hr) • Destruction toughness $K_{IC} > 6 \text{ MPa} \cdot \text{m}^{1/2}$ 	<p>Modified model for static blades, secondary model for heat impact destruction tests, strength verification for cutoff test samples</p> <ul style="list-style-type: none"> • Instant destruction ≥ 400 MPa (1,400°C) • Delayed destruction ≥ 250 MPa (10,000 hr) • Destruction toughness $K_{IC} > 3 \text{ MPa} \cdot \text{m}^{1/2}$
Molding	<ul style="list-style-type: none"> • Grinding efficiency 100 mm³/mm·sec, grinding ratio 6,000 drop in strength for nongrindable material < 15% • Surface coarseness: 0.3 μm R_a Dimensioning accuracy: 5 μm • Surface condition for working hardness change $\pm 5\%$ residual compressive stress 	
Bonding	<p>C-C: 1,250°C, 80% of substrate C-M: 400°C, 200 MPa Residual strength 80% after 1,000 temperature change for normal temperature ~400°C</p>	<p>C-C: 1,400°C, 80% of substrate C-M: 500°C, 200 MPa Residual strength 80% after 1,000 temperature change for normal temperature ~500°C</p>

3.2 Development of Material Techniques

It is predicted that ceramics, as future high-temperature structural materials, will be required to have higher performances and be able to endure more severe environments. New studies on the "development of material technologies" targeted at improved toughness against destruction, acid resistance, and abrasion resistance were implemented in Phase Three. Emphasis was placed on the development of toughened materials or surface strengthened materials that use silicon nitride or carbide as the matrix. Some of the material qualities targeted in the research are listed in Table 4.

Three material toughening methods were studied: particle dispersion method, fiber-reinforced method, and crystal control method. In the particle dispersion toughened material, the complex powder is synthesized by dispersing fine particles of its second phase constituent in either the silicon nitride or the carbide substrate material which is then toughened by sintering. Toughening was confirmed to a certain extent but not all the targeted performance was achieved. Since the strengthening and toughening mechanism in

Table 4. Example of Target Performance in Development of Material Technology

Material/ technique	SiN matrix	SiC matrix
Particle dispersion high toughness	$K_{IC} \geq 12 \text{ MPa} \cdot \text{m}^{1/2}$ $\sigma_{1250} \geq 600 \text{ MPa}$	$K_{IC} \geq 7 \text{ MPa} \cdot \text{m}^{1/2}$ $\sigma_{1400} \geq 400 \text{ MPa}$
Fiber- reinforced high toughness	$K_{IC} \geq 15 \text{ MPa} \cdot \text{m}^{1/2}$ $\sigma_{1250} \geq 500 \text{ MPa}$	$K_{IC} \geq 8 \text{ MPa} \cdot \text{m}^{1/2}$ $\sigma_{1400} \geq 300 \text{ MPa}$
Surface coating techniques	<ul style="list-style-type: none"> • Static oxidation resistance (1,000~1,400°C) (30% saturated) • Abrasion-resistant property (1 order > substrate) 	<ul style="list-style-type: none"> • Static oxidation resistance (1,000~1,400°C) (\geq substrate) • Abrasion-resistant property (1 order > substrate)

the fiber-reinforced material is understood to a certain extent, the quality of the material set is significantly higher and hence, a material with higher performance absolute values was achieved. However, the current situation is that the targeted performance is not entirely satisfied.

In the surface strengthened technique, the acid resistance and abrasion resistance of the ceramics is improved by altering the surface quality of the ceramics by ion insertion or covering by chemical vapor deposition (CVD). By creating a layer of silicon nitride or carbide on the ceramics surface by CVD, the weight increase due to oxidation at 1,300°C became one order of magnitude lower than the base substrate. The material was also confirmed to be stronger in four-point bending tests. The techniques obtained in this project will be applied to the still and dynamic wing models studied in the final compilation phase.

3.3 Evaluation and Application Techniques

Evaluation and application techniques continued from Phase Two. Emphasis was placed on nondestructive inspection techniques, creation of design standards for application of ceramics to turbine parts, analysis of destruction factors under mechanical or thermal environmental conditions, warranty testing methods for ceramics material and the creation of warranty standards for turbine parts.

4. Conclusion

The Fine Ceramics Project has already entered the R&D compilation phase and is currently in the midst of creating model configurations for still and dynamic gas turbine wings as a means of compiling the materials and technologies achieved through the various phases of the project. Their performance will be proved in FY 1992, the final year of the project. The research consortium and the national research institutes are in close liaison in the pursuit of superior results. Much effort is also expended in the development and expansion of evaluation and application techniques in the use of ceramics as a high-temperature structural material. The world will focus on the results of these efforts. One result of the Jisedai Project is the edge it gave Japan's fine ceramics related techniques over the rest of the world and even after completion of this project on R&D of ceramics for use in high-temperature structures, Japan will be expected to continue taking the lead in R&D in all phases of society—industrial, academia, and government.

Future Trends in Fine Ceramics Research

926C0071L Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 83-87

[Article by Masahiko Shimada, professor, Molecular Chemistry Engineering Department, Tohoku University]

[Text] 1. Introduction

It is recognized that the creation of new materials is the key to research and development of advanced science and technology. The discovery of new materials will play a leading role in the development of advanced technologies. A recent example would be the discovery of high-temperature superconducting oxide ceramics. In this manner, the discovery of new materials strongly impacted the R&D sector and contributed significantly to progress in science and technology including related fields.

Fine ceramics is a new material that has received a lot of attention. Japan produced significant results in R&D in fine ceramics including functional ceramics and ceramics for structural use. Functional ceramics used in electronic parts currently forms the basis of the industry. R&D on structural ceramics is basically for nurturing Japan's industries. As a result, some of these research efforts were marketed and Japan now leads the world in studies on fine ceramics. Further advances in the development of fine ceramics would require R&D from new standpoints and should not stop at improving performance along conventional lines. Development of higher performance fine ceramics requires work on existing material properties; in other words, system expansion for solid solutions, creation of high performance fine ceramics like the development of new complex materials through atomic nanolevel or micro/macro level structural control, addition of functions to structural ceramics or the toughening of structural ceramics, or the creation of new matter. Studies were also made on possible combinations of elements in the Periodic Table to create compounds with differing crystal structure, molecular structure or arrangement. As a result, recent advances made in synthesizing matter and methods to measure properties has enabled effective design and search for new matter. A specific set of functions are required when making devices with these new materials and the creation of high-performance materials is now recognized as an important R&D field.

2. Methods To Develop New High-Performance Materials

The different approaches to developing new high-performance materials are illustrated in Figure 1. The typical ones are described below.

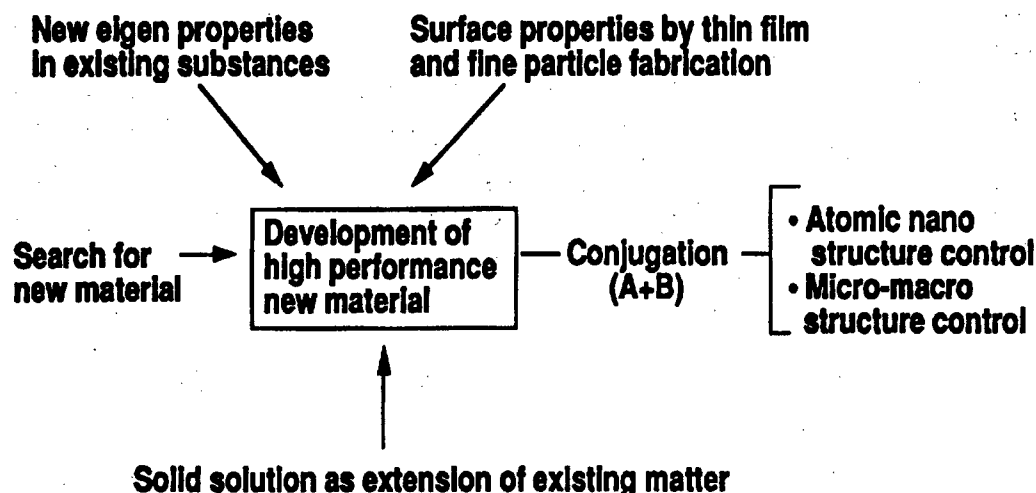


Figure 1. Multi Approach Example of Development of High Performance New Material

- 2.1 **New intrinsic characteristics in existing materials:** There is always the possibility of new properties being discovered although existing properties of the material have already been measured and reported or as a result of improvements in measuring techniques.
- 2.2 **Unique characteristics when making material into fine particles or thin film:** By making an existing material into ultrafine particles or thin film, new properties like surface functions or structure properties can be created in the material through surface activation due to an increase in the specific surface area.
- 2.3 **Conjugation:** There are several examples of research on macro conjugations for expressing synergistic effects by combining existing masses together. A multicrystal sintered mass, however, is a kind of micro conjugate when considered from the microstructure standpoint of its particles and grain boundary phase. For example, the variable resistor property not evident in the constituents of an N type semiconductor, ZnO and insulator Bi_2O_3 was observed in the conjugate. The properties of the multicrystal sintered mass can be diversely altered by controlling the grain boundary phase and therefore holds the key to the development of new functional materials. Research on both micro and macro nano conjugates has been very popular in recent years. R&D on new functional materials like interparticle-dispersed toughened ceramics, artificial lattice, interlaminary conjugates with organic/inorganic mass intercalated between the laminated compound. The latest material currently being focused on is the complex functionally gradient material,

particularly that with metal and ceramics as the terminal mass, while the center strata is filled with a terminal matter with continuous gradient eigen property. In this manner, development of new materials can be extended to include not only structural but also functional materials.

The most important point in the development of high-performance fine ceramics by conjugation is element technology for structure control. R&D for new fine characteristics by atomic nanolevel structure control and/or micro/macrolevel structure control can be performed through the creation of a high-level structure/controlled fused material in a nanolevel structure controlled matrix.

- 2.4 Solid solution as an extension of existing substances: Positive or negative ion replacement type complete solid solution can be fabricated if the radii of the atomic ions that constitute the characteristic two terminals of the inorganic compound have the same crystal configuration are similar. When the aforementioned conditions are not satisfied, partial replacement type solid solutions will be fabricated in the vicinity of the terminal constituent. An example of the latter is yttrium eutectic tetragonal zirconia (Y-TZP)--commonly known as high-strength tetragonal zirconia--and heat-sensitive resistor PTC thermistor $(\text{Ba}, \text{La})\text{TiO}_3$. Curie temperature of complete solid solutions can be freely switched from 30°C to 300°C depending on the quantity of Ba ions in the strong BaTiO_3 dielectric with Sr or Pb ions.

Partial replacement of (BaSr) or (BaPb) with La ion allows fabrication of the high-performance thermistor. Complete solid solutions that consider atomic ion distribution include manganese zinc ferrite solid solution that contains positive spinel ZnFe_2O_4 and negative spinel MnFe_2O_4 . Successful fabrication of superior magnetic head material was achieved through increment of the saturation magnetism for increased magnetic inductance. In other words, decrement of magnetic anisotropy and magnetic distortion was achieved by altering the value of X in the $(\text{Fe}^{3+}_{1-x}\text{Zn}^{2+x})(\text{Fe}^{3+}_{1-x}\text{Mn}^{2+x})\text{O}_4$ solid solution. Although solid solutions cannot be designated as a new substance, properties can be enhanced or incorporated into existing materials to achieve completely different and new materials. An example is the primary and secondary photoelectric effects in PLZT. This may be a boring and tedious job for researchers who deal with material synthesis but it is nevertheless a very important development tool in the field of new-function and high-performance materials development.

Solid solution ceramics was widely studied because of the high performance of functional ceramics. However, unlike the field of functional ceramics like β -sialon or α -sialon, studies to improve performance using solid solutions virtually do not exist, with the exception of Mg-PSZ as a form of Y-TZP or partially stabilized zirconia. Solid solutions for functional ceramics are mostly positive ion replacement type and studies on negative ion replacement type solid solutions in ceramics for

structuring applications will be most interesting since chemical bonding is believed to be the major factor behind function expression.

- 2.5 Search for new substances: The synthesis of new high-performance materials is a most attractive theme for those involved in material development. Development of new materials will, as is known in the development of high-temperature superconducting ceramics, strongly impact the fabrication of a diverse number of other substances.

3. One Example of Search for New Substance

The probability of creating a whole new substance is extremely slim as it can be thought of as a random mix of various elements in random quantities and synthesized by various methods. As a result, new substance design (lattice design) tools that employ knowledge on atomic size, electronegativity, electron number chemical bonding, and crystal structure were studied. Let us use the Periodic Table to illustrate this.

A Group IV element semiconductor like Si or Ge has the same structure as diamond. Boron nitride (BN) is a Group III-V compound with properties that are extremely similar to carbon and as a result, can be synthesized into graphite structures or when under ultrahigh-pressure conditions, into CBN whose structure is similar to diamond. Isoelectrochemical compounds with Group IV elements include Group III-V compound semiconductors like AlN, AlP, AlAs, GaN, GaP, and GaAs and Group II-VI compound semiconductors like ZnS, ZnSe, CdS, and CdSe. The Group VI element substances like the Group III-V and Group II-VI compounds have simple valence laws. In other words, the "octet" law holds. Since synthesis of new substances is possible from these and from their combination with those elements which are in nonsymmetrical positions to the Group IV elements, they are termed "periodic compounds." For example, B_2O is a periodic compound made of boron (Group III element) and oxygen (Group VI element). B_2O with a graphite or diamond structure can be synthesized when done under high-pressure conditions. A new B_2O substance can therefore be fabricated. Oxidation of BP at 6 GPa and 1,100°C will create a substance that resembles the trigonal configuration in diamond structured B_2O where lattice constants $a = 0.2879$ nm, $c = 0.7052$ nm, and density = 2.48 g/cm³, Vickers hardness = 40 GPa. ZnP_2 and B_2S were also synthesized as periodic compounds. The search for periodic compounds with photoelectric transforming functions observed in Group III-V or Group II-VI compound semiconductors looks promising. Studies have recently become particularly active on synthesis of $CuInS_2$ or $ZnSnP_2$ with chalcopyrite or distorted zinc blende structure in attempts to develop high-performance materials using their semiconductor properties. About 40 substances were synthesized. These compound groups can be assumed to be periodic compounds by considering their chemical composition as twice that of Group II-VI compounds and written as II_2VI_2 or when split into Group I and III elements that are symmetrical with Group II elements, written as I III VI_2 . $CuInS_2$ is an example. When Cu and In atoms are arranged regularly, its structure becomes tetragonal chalcopyrite but when they are irregularly arranged, it assumes the cubic distorted zinc blende configuration. By a similar argument for the chemical equation for III_2V_2 , $ZnGeP_2$ or

ZnSiP_2 can be assumed to be II IV V_2 compound by splitting the Group III elements into Groups II and IV elements. Regular and irregularly configured Zn and Si (Ge) will assume chalcopyrite and distorted zinc blende structures, respectively.

Periodic compounds based on Group IV elements and their extended systems of I III VI_2 compound groups can be developed into new material groups with diverse semiconducting properties with the help of replacement solid solutions observed in Group III-V or Group II-VI compounds or by introduction of a similar tool in the form of covalent bonding or ionic bonding.

4. Development of Structure Control New Fusion Fine Ceramics

The current direction in research and development in feasible ceramics for structuring applications is reliability. This can only be achieved through significant increased de-struction toughness in current fine ceramics and strength, particularly high-temperature strength. Improvements can be achieved through control of the grain boundary structure in monolithic materials while reinforced toughness in conjugation techniques which include micro conjugation of particle dispersion, whisker dispersion and long-fiber reinforcement, and nano conjugation by dispersing differently shaped nano sized substances in particle or grain boundary. Although current research uses various conjugation techniques, a new multitoughening technique (a combination of various conjugation and toughening techniques) that includes reinforcement of monolithic materials is being developed. The establishment of structure control factor techniques is important in the development of new fusion fine ceramics. Structure control at the atomic, nano, micro, and macro levels are important. An important issue is the development of micro level structure control techniques for dispersing whiskers or particles in nano level composite matrixes. Although ceramics and metal bonding techniques are important for realizing fine ceramics, highly-reliable bonding techniques are still not available (particularly, parts under high temperatures). Such bonding techniques were recently studied as part of the research on functionally gradient materials.

Fine ceramics were classified as functional and structural materials for the sake of simplicity but this boundary is becoming less distinct. This type of distinction is inappropriate in this age of particle or grain boundary control in the ceramics at the atomic or molecular level. In the future, the distinction between structural or functional use should be removed. In the same manner, distinctions between ceramics, metal, high polymer or even natural substances should be successively removed in the development of new materials.

5. Conclusion

Application environment for fine ceramics will become more and more severe in the future, and environment resistance will be a required property in materials. Mechanical properties will become more important in functional ceramics. On the other hand, chemical stability like oxidation resistance will be required in structural ceramics.

Issues like solid phase reaction and grain growth at high temperatures above the working temperature of 1,300°C will become important. The objective is the diverse development of high-performance fine ceramics through further introduction of toughening mechanisms in dispersion systems where chemical reactions do not occur or in oxide ceramics that are chemically stable.

Results of High-Performance Crystal Control Alloy, Complex Materials

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[Article by Kenichi Matsuno, deputy director, Mechanical Engineering Laboratory]

[Text] 1. Introduction

For eight years stretching from October 1982 to March 1989, research and development was conducted on "high-performance crystal control alloy" and "complex material" under the Jisedai Project. In the former, three national research institutes and seven corporations participated while in the latter, six national institutes, 12 corporations, and three universities participated. R&D was outsourced to corporations and universities from the Research and Development Institute of Metals and Composites for Future Industries which was specially established.

The purpose, process, and results of the project are described below.

2. Crystal Control Alloy

2.1 Research Purpose

High-performance Ni-base single crystal alloy and Ni-base alloy reinforced by dispersed particles were developed for use in movable blades of gas turbines and jet engines which require extremely high-heat resistance. At the same time, research was also done on production techniques for turbine blades made from the developed alloy. Development of Ni-base ultraplastic alloys and ultraplastic strengthened Ti alloy for use in turbine and compressor disks as well as its process technologies were also performed.

The targeted performances for each alloy developed are as follows.

(1) Ni-base single crystal alloy: Creep fracture life: 1,000 hours and fracture elongation: 10% at 1,040°C, 14 kgf/mm²

(2) Ni-base ultraplastic alloy: Tensile strength: 160 kgf/mm² at 760°C; fracture elongation: 20% and exhibits ultraplasticity at around 1,100°C

(3) Ni-base particle dispersed strengthened alloy: Creep fracture life: 1,000 hours and fracture elongation: 5% at 1,100°C and 14 kgf/mm²

(4) Ultraplasic strengthened Ti alloy: Specific strength: 28 (kgf/mm²)/(g/cm³) at 300°C. Elongation: 10% and exhibits ultraplasicity at around 900°C.

2.2 Overview of Research Results

2.2.1 Ni-base single crystal alloy

Ni-base single crystal alloy was developed for fabricating air-cooled turbine blades from single crystal alloys which are superior to unidirectionally solidified column crystal alloys.

A computer was used to design the alloy. Several types of alloys that satisfy the targeted values mentioned above were successfully developed by controlling the combination of the strengthening elements. W or Ta, the quantity of γ' phase and the difference (mismatch) between the lattice constants of the γ' and the γ phase.

Very pure fused silica was used as the basic constituent in the filler for casting air cooling blades. A filler with superior heat resistance, low contraction rate during firing and which can be easily removed after casting by dissolving in an alkali was successfully fabricated by controlling its granularity, extrusion molding the raw material that contains crystallized ceramics and finally, by improving the annealing patterns.

Simulations on solidification were used to analyze and test casting of hollow single crystal blades. Experiments like application of remelted melting stock to plasma scull melting and the attachment of a complementary heater to the casting furnace were performed. Finally, a good hollow single crystal turbine blade (about 90 mm in length) made of a developed alloy and filler was successfully fabricated. Recycling of scraps from ceramics filter was also tested.

2.2.2 Ni-base ultraplasic alloy

The objective is to make materials used for fabricating large, complex-shaped objects like gas turbine disk by ultraplasic casting of hot isostatic pressing (HIP) preform of high γ' phase alloy powder excluding the extruding process.

Various types of alloys designed by this method described previously, were proposed. The characteristics improved and approached those targeted. In the end, all properties except the ultraplasicity did not clear the targeted values. (It can be assumed that the targets set were too high.).

An ultrafine powder was trial produced by dropping the solution onto a high-speed rotating plate and rapidly cooling by liquid helium or by the Ar gas spray method. The former method produced finer powder. The gas spray powder

method succeeded in casting an ultraplastic disk 400 mm in diameter from a preform made by HIP alone.

The powder was fractured by an attritor (strong forced-stirred bowl mill) and then made finer by recrystallization thereby improving its ultraplasticity after solidification during HIP. It was found that ultraplastic molding by HIP alone is possible although the granularity of the powder is slightly large.

On the other hand, facilities, funds, and time are required for conventional ultraplastic casting in an inert environment using an Mo alloy mold. New ways to improve casting and other mold materials were also studied. As a result, a method to cast preform inserted in a carbon steel sheath under normal atmospheric conditions as well as the effectiveness of the ceramics mold were proved. Studies were also made on the solid phase bonding using the ultraplasticity of rapidly solidified Ni-base superalloy thin film. Although this study differed slightly in purpose from others, strong bonding was observed in the thin film that has cast Ni-base alloy as the bond.

2.2.3 Ni-base particle-dispersed reinforced alloy

This is a strong ultraheat-resistant alloy developed by dispersing an oxide (yttria fine particles) in $\gamma + \gamma'$ alloy and fabricated into turbine blades by casting and unidirectional recrystallization.

The alloy was developed by the aforementioned alloy design method. This alloy displayed a 4 percent increased lifespan of 3,500 hours that significantly exceeded targeted values. Particle-dispersed reinforced alloys are weaker than single crystal alloys at mid-temperature ranges of around 800°C. This was improved by designing an alloy with many γ' phases.

Good extruded bars were fabricated by controlling precision mechanical processes followed by molding by extrusion. However, test casting of such bars at room temperature into complex shapes (those with large variations in cross section) were found to be difficult. There were problems with recrystallization and the fabricated shapes were not sufficiently strong thus requiring the introduction of a certain amount of mechanical molding.

Superior configurations were successfully fabricated by annealing within a temperature range, the complex shaped unidirectional recrystal cast in a halved hollow vessel. However, its connectivity is not so good.

2.2.4 Ultraplastic reinforced Ti alloy

This alloy has superior ultraplastic molding properties and is used for fabricating complex shapes like the disks in compressors of jet engines. It is developed from Ti alloy with a relatively high specific strength and ultraplastic cast after HIP treatment of its powder.

This alloy-designed alloy well exceeds targeted values and we have been successful in developing several types of alloys with superior ultraplastic properties.

Powdering was achieved by the plasma beam centrifugal atomizing method. Ultrafine powder with low contamination was successfully produced. The HIP material made from such powder displayed good ultraplaticity and cast models of a bladed disk 150 mm in diameter as well as a boss disk model 40 mm in diameter were successfully fabricated. Properties of these cast models were also superior.

3. Complex Materials

3.1 Research Target

Research ranging from material development to raw material fabrication, molding techniques and quality assessment was carried out to develop heat-resistant complex materials (for use in structures) and their applications assuming large space structures, aeronautic structures, turbine engines, and automobile structures are advanced applications and the target is the development of fiber-resin or fiber-metal complex materials (fiber-reinforced plastic (FRP)), fiber-reinforced metal (FRM)) that are lightweight and show strength, toughness, and heat-resistant properties that meet the demands of the application."

In the basic project, the targeted performance in the standard testpiece for the tensile strength along the fiber alignment at room temperature for a 90 percent reliable fiber and for the heat-treatment temperature that retains 90 percent of that strength was as follows:

- (1) Resin complex material (FRP): Heat-resistant temperature: 250°C
Tensile strength: 240 kgf/mm²
- (2) Metal complex material (FRM): Heat-resistant temperature: 450°C
Tensile strength: 150 kgf/mm²

3.2 Overview on Research Process and Results

3.2.1 Research process

The development of heat-resistant matrix resin was the main objective and as a result, research to improve the heat resistance, water resistance, and workability of various resins, the development of new matrix resins and trial production of unidirectional carbon fiber soaked tape (prepreg) were carried out.

Basic research was carried out in molding technologies. Initially, advanced complex materials were fabricated into aircraft, automobiles, and space-related structures by about 10 different existing molding techniques followed by studies to improve the reliability and productivity of these processes. In the later stages, development shifted from the autoclave laminating techniques to more revolutionary molding methods and basic technical studies were also done on new press mold methods that target interlaminary reinforcement of laminated structures.

The metallic complex wire was developed by homogeneously soaking an aluminum matrix, to act as a filler, in a fiber bundle of carbon and silicon carbide fibers developed in Japan and used as a reinforcement in FRM, which could thus be commercialized.

Parallel to that, studies were also done on applications of existing molding techniques like press, roll, HIP, and hot extrusion methods to FRM which contains various reinforcement fibers including the wire developed above. In the later stages, the laser roll molding technique that aims at continuous production of thin complex materials, was developed.

Design technologies included the establishment of development targets for complex materials and the development of design methods for complicated shapes that employ directional properties in mechanics. Product quality assessment techniques included the development of testing methods and evaluation methods for the static and dynamic characteristics, defect detection, process control, reliability analysis, and environmental monitoring for the material, process, structure factors and operating environment. A fact database was also created for storage, retrieval and statistical analysis of the test results.

3.2.2 Results

(1) Achievement of target performances

The tensile strength data of the standard testpiece at room temperature and high temperature was statistically treated. The lower limit (B value) of the 90 percent reliability value satisfied the aforementioned target.

(2) Positioning of results when material is considered heat resistant

The target performance was the tensile strength along the fiber alignment. The exceedingly high specific strength and specific elasticity are the strong points in a complex material. Carbon fiber-reinforced plastic (CFRP) has a significantly higher specific strength than existing metallic materials when employed at temperatures up to 250°C. Up to 450°C, FRA1 is best while above that, FRTi becomes advantageous.

(3) Development of highly workable heat-resistant matrix resin

Three types of matrix resins (epoxy base), polyimide base, and polyquinoxaline base) which are very workable and heat resistant, were developed. The properties of these resins far exceed those of existing materials—room temperature and hot/wet compression strengths, toughness to destruction are particularly superior. Their fatigue and impact strengths exceed those of existing epoxy resin types.

(4) Development of basic FRM techniques that take advantage of locally produced materials

Polyacrylonitrile (PAN) base and pitch base carbon fiber/pure aluminum, silicon carbide fiber/pure aluminum and aluminum doped with 5.7 percent Ni, complex wires were developed for use as FRM filler. As a result, FRM molding

that is almost similar to aluminum wire molding became possible. Heat-resistant FRM with heat-resistant aluminum alloy, stabilized titanium alloy matrix and SCS base vapor deposited silicon carbide fiber were also developed.

(5) Development of molding techniques--Property assessment tests

Laminated single body molding, continuous molding of duct-die material and rapid hardening molding methods were established for fabricating FRP into existing shapes. New techniques were also developed to replace the existing autoclave method. They include the highly efficient and high-performance high-temperature liquid pressure molding method, microwave method, three-dimensional weaved resin-soaking method and the magnetic field press method.

Basic techniques like the roll multiple connection molding method for producing large sheets, hot press molding method for three-dimensional parts, HIP precision molding and laser roll molding method for materials for fabricating thin and long parts were developed for FRM. Assessment tests were also developed to determine static and dynamic basic properties in the search for optimum conditions for each type of material.

(6) Development of product quality assessment--Development of design techniques

Product quality assessment techniques like management and control of molding process (automatic detection of hardening reaction, automatic discernment of molding cracks), various defect detection techniques besides methods for assessing properties of complex materials, were developed. Environment-friendly devices were developed and test produced. An optimum design program was developed and verified. Revolutionary structuring methods were developed. Targets in material development were established while structure analysis methods and impact-heat stress analysis methods were also studied thus enabling the realization of advanced complex materials.

(7) Database development

A complex material database system (PRODACOM) was created and test data stored.

(8) Others

Intangible results include the rapport and interaction between material manufacturers and users through joint development and study programs as well as the expertise accumulated by the material manufacturer.

4. Conclusion

R&D on "high-performance crystal control alloy," "complex material," materials and their processes published results that met world standards are now established basic technologies. In all cases, industrial patents resulting from this R&D far exceeded 100 while the knowledge and expertise accumulated cannot be counted. Product development will be necessary in the future.

The overwhelmingly great number of successes were published in the High Performance Crystal Control Alloy Technology Handbook (February 1991), and the Next-Generation Composite Materials Technology Handbook (July 1990) by the Japan Industrial Standards Association (JIS).

The international exchanges that developed during the eight years of research and development also deserve special mention. This project has greatly contributed to globalization of research efforts—a theme of the 21st century.

A total of about 600 researchers participated in this project. Besides the above-mentioned participating organizations, numerous other national research centers, corporations and universities also contributed to the project. Invaluable counselling was received from members of the assessment board. I would like to take this opportunity to express my gratitude to the researchers attached to the participating organizations, cooperating bodies and the members of the assessment board.

R&D in Intermetallic Complex Materials

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[Article by Haruhiko Kondo, director, Metal Department, Government Industrial Research Institute, Nagoya]

[Text] 1. Introduction

Space and aeronautical projects like the space plane and the SST/NSTA and energy projects like coal gasification power generation plants and nuclear fusion will carry us into the beginning of the 21st century. The realization of structural materials whose heat resistance, high specific strength, high rigidity, and oxidation-resistant properties under extreme conditions will be vital for the realization of these projects since existing materials do not exhibit such properties. The development of a lightweight material with a high melting point that can withstand high temperatures of more than 1,000-2,000°C are particularly vital for use in space plane structures, movable blades in gas turbines and walls in nuclear reactors.

This project which began in FY 1989 concentrates on the development of space and aeronautics and energy-related equipment and devices as well as the establishment of basic technologies related to the properties of intermetallic alloys under high-temperature conditions—a substance that has heat resistance, high specific strength, high rigidity, and oxidation resistance.

2. Metallic Material With High Specific Strength and High Melting Point

The high specific strength common in all new materials will be the focus of development as this factor will contribute to the improvement of the earth's environment and energy effectiveness. In general, metals are relatively heavy. As a result, development to date concentrated on those with high specific strengths—Ti, Al, Mg alloys and complex materials. However, these materials are not very heat resistant and, as a result, development shifted to intermetallic materials that use such lightweight metals as the base.

Fine ceramics was developed for use as a structural material with a high melting point, but the demand for a more reliable and tougher material resulted in a shift to development of intermetallic materials that contain heat-resistant metals and toughened through conjugation of fine ceramics.

Intermetallic alloys have properties that are halfway between ceramics and metals and depending on the application, the advantages of both materials can be employed. It is still a relatively new product with a history that goes back only about 10 years and is now rapidly being developed based on the proposal for application under extreme conditions.

3. Project, Research Themes, and Organization

This project began around 1987 with the feasibility study on intermetallic alloys by the Metal Subcommittee of the Research and Development Institute of Metals and Composites for Future Industries (RIMCOF). Results of this study were published in September 1988 under the title "Current Status and Future Issues in Development of Ultra-Environment-Resistant Advanced Materials." Then in March 1989, "Intermetallic Alloys for Fabricating Structures" was published. These publications are the fruits of joint efforts between researchers from 17 industrial, three academic, and three government organizations that are interested in intermetallic alloys. Of the alloys studied, Ti-Al base (high specific strength intermetallic alloy) and Nb-Al base (high melting point intermetallic alloy) are described below.

The overall planning for the project was divided into two phases—four years each. Material design for intermetallic alloys was done in Phase One. Fundamental considerations on production and process techniques were also made. Phase Two applies the results of Phase One to upgrade the material design and establish better production and process techniques.

Investigation studies were also done by researchers from national research institutes with guidance from the casting and smelting division while hearings on research proposals from those organizations desirous of participating in the project were held as the project progresses. This project was funded by the New Energy Development Organization (NEDO) with six corporations and three national research institutes participating. Another three corporations (one foreign corporation) is scheduled to join the project in FY 1991.

4. Target and Its Significance

In intermetallic alloys with high specific strength, the final targets are specific strength (strength/specific weight) of 100 MPa at 1,100°C and elongation of 3 percent at room temperature. TiAl is a potential candidate material because of its light weight, high strength which does not deteriorate even at high-temperatures, high heat resistance, whose L10 crystal lattice configuration is relatively simple and allows plastic deformation.

The high Al side of the chemical quantum configuration of Ti:Al = 1 has a wide eutectic range. TiAl on the high Al side is extremely brittle so that the low Al side should be employed as the structuring material. TiAl, however, peels and configuration control techniques like reduction of the crystal configuration or conjugation are essential for neutralization of this effect. The low rollability of TiAl at normal temperature is also a problem. Additives like V and Mn are used to decrease the deformation stress and prevent stress nodes (concentration of stress at one point) thereby promoting bicrystal deformation.

The direction is not necessarily fixed in alloy design and new studies are vital. Development of TiAl assumes potential application as a lightweight heat-resistant material for use in next-generation aircraft and as a heat-insulating structural material.

The final target for high melting point intermetallic alloys are tensile strength of 75 MPa at 1,800°C, and elongation of 3 percent at normal temperature. Fine ceramics are being developed as ultrahigh-temperature materials but another candidate proposed is the intermetallic alloy which has the toughness and reliability of metals. The intermetallic alloy singled out is Nb₃Al which was studied as a functional superconducting material and is practically ignored in the field of high-temperature structural materials. High hopes and at the same time high risks are thus involved in its study. Nb₃Al has a high melting point (1,960°C) and its regular configuration does not deform even when heated to very near its melting point. Since its crystal configuration is relatively complex (Al₅), it is very brittle at room temperature and is also very difficult to mold.

5. Details and Results

The project is nearing its third year and Phase One is now entering its last stage. Below are some of the more spectacular results.

5.1 R&D on High Specific Strength Intermetallic Alloys

Three national research institutes studied the basic configuration and properties, base powdering techniques, synthesizing by stirring and mixing and configuration control techniques. Three private research centers investigated material design and ways to fabricate thin sheets directly from the melt.

Configuration control and oxidation properties were studied through phase transformations during heat treatment and thermomechanical processing (TMP) during room temperature casting. Configuration control is achieved by heating to 1,350°C and 1,200°C. Ti-48at%Al casted slab (ultrafine laminated configuration) base and the $\alpha + \gamma$ (TiAl)₂ phase. It was confirmed that the slab assumes 1) a lamellar configuration with layers of α phase and γ phase; 2) a mixed lamellar particle and particle configuration whose sizes are almost similar; 3) subtransus configuration where lamellar configuration transforms to mixed particle configuration; 4) near γ single phase where almost only γ particles exist. The mechanical properties of these configurations differ—the bigger the volume ratio (change within 0-80 percent range) of the γ particles, the more effective rollability at room temperature can be improved.

Material configuration of various Ti-Al cast slab whose Al weight content varies from 44-52 at% and heat treated to 1,200°C/86.4 ks, varies with the Al content. It is classified as follows: When Al content is higher than about 50 at%, it is a) γ particle + α^2 (Ti₃Al) particle, and when 47-50 at%, it is b) γ particle + γ/α_2 lamellar particle + α_2 particle and γ particle decreases with Al content and lamellar domination increases. Below 46 at%, the whole becomes c) γ/α_2 lamellar particles. Molding of all these materials at room temperature produced iso-axial γ and α_2 particles of 5-300 μm , which was accompanied by

dynamic recrystallization. It was confirmed that the Al concentration must be about 46 at% to produce ultrafine iso-axial crystals.

Molding and sintering methods like the TiAl powder ejection molding method was studied and will be applied to the fabrication of complicated shapes. Ejection molding conditions (cylinder temperature 145°C, ejection pressure 120 MPa, ejection speed of 130 ml/sec) were identified and applied to a tensile testpiece. The current status is that TiAl powder appropriate for ejection molding does not exist and shape, particle size and impurity elements (oxygen, in particular) are not satisfactory. This study employed powder particles with an average diameter of 16 μm , nonspherical in shape and an oxygen content of about 1 wt%. Activated TiAl oxidizes during skimming and annealing and thus must be heated in vacuum. The effect of heating during skimming on shrinkage, density, and oxygen content was confirmed. Observations of the internal configuration after annealing showed that heating to above 1,400°C is essential. In this case, $\gamma + \alpha_2$ layer was produced but its tensile strength at room temperature was low—below 300 MPa. This is because of the generation of Al_2O_3 due to selective oxidation of Al with the oxygen content. Thus, control of the oxygen content in the powdered raw material is very important. Supply of powders suitable for ejection molding will be the main issue in the future.

The half-melted metal is stirred at high speeds to create chunks of ultrafine crystal particles. A synthesis stirrer test device was created by using a model material (Cu-Al) to determine its specifications. This device dissolves TiAl in a high frequency inductive furnace—calcium crucible. The melt is then poured into a hexagonal rotator (max 5,000 rpm) and spun at high speed to make it into a frozen slurry condition by rapid cooling and solidification of the liquid drops. It is then crushed. This is then frozen. Cast chunks produced this way have ultrafine crystal particles that are less than 1/50 the size of normal chunks. Tests on the model material proved that the strength of the material produced by this method is about two-thirds less hard than normal cast materials. Rollability and toughness can also be improved. Powder and thin film materials were used in the configuration control method where bulk-ing is performed while the configuration is controlled. Material production processes are currently being developed to enable creation of high performance TiAl.

Material design studies concentrated on equilibrium diagrams of Ti-Al-X where X is the third element doped into Ti-Al. Studies on material design for Ti-48at%Al-2at%X are currently in progress. Elements like V, Cr, Mn, Nb, Mo, and Ta were selected as effective additives for improving the normal temperature rollability and high-temperature strengths of this intermetallic alloy. All these elements exist as iso-axial particles with partial $\gamma + \alpha_2$ lamellar configuration in the cast chunks but transforms when uniformly heated. The lamellar configuration in the intermetallic alloy with V, Cr, Mn, and Nb additive disappears and transforms into about 200 μm of iso-axial γ particles. On the other hand, the lamellar configuration in the alloy with Mo or Ta additive did not transform at all. Crystal particle became finer during recrystallization that accompanies normal temperature casting. V, Cr, Mn, and Nb reduces the size of the γ particle and at the same time, a faint third phase (β -Ti phase) besides the α_2 and the γ was confirmed near the crystal

grain border. The percentage of β -Ti phase in the alloy with Mo additive was extremely high and this indicates that Mo is a very strong and stabler element even in TiAl. This material will thus be effective for improving the workability at high temperature and at the same time produce finer crystals. The alloy with Ta additive cannot be recrystallized and the molded material only had lamellar configuration. The mechanical properties of alloys with Ta and Nb additives are highly promising but have not achieved the target yet.

The method to fabricate thin sheets directly from the melt consists of two techniques—fundamental production technique for making thin sheets of TiAl whose configuration is controlled and fundamental technique for secondary molding of the thin sheets. Thin sheet fabrication was done by hot press using an environment-controlled sheet caster, room temperature hot press while secondary molding is achieved under ultraplastic molding in an inert environment. Thin sheet fabrication studies used Ti-51at%Al ($\gamma + \alpha_2$ on equilibrium diagram) and Ti-46at%Al (single γ phase) which have differing solidification speeds. Heat-treatment conditions before hot molding were investigated. Studies on the mechanism of high-temperature deformation showed that $\gamma + \alpha_2$ laminated configuration has a relatively higher resistance to high-temperature deformation than γ single phase. The effects of dendrite arm spacing which changes with the solidifying speed, is also smaller. The resistance to deformation in both configurations was found to have a strong dependence on deformation temperature and strain velocity. A configuration map was made for the recrystallization of the material transformed at high temperature. The γ single phase material was found to recrystallize very easily by molding and then heating while the $\gamma + \alpha_2$ two-phase material does not recrystallize unless it is heated to single phase temperature range (1,400°C).

Investigations on secondary molding of TiAl concentrated on plastic deformation characteristics. It was confirmed that iso-axial ultrafine particle production is very important. Studies were made on the dependence on crystal particle size of plastic workability of iso-axial material whose particles have been controlled to 20-100 μm , and on configuration changes during deformation. The dependence of plastic deformation of Ti-48at%Al-1at%Mn with little γ phase on particle size decreased during dynamic recrystallization while deforming. On the other hand, particles of Ti-46at%Al which contains relatively large amounts of α_2 become finer during material fabrication. Configuration stability after the high-temperature deformation increases thus confirming its superior plastic deformation properties.

5.2 R&D on High-Melting Point Intermetallic Alloys

This was studied by two national research institutes. Configuration and properties were identified. Basic techniques that contribute to the powder shape are also investigated. Four private research centers studied material design, precision casting methods, and alloy powder molding methods. It is a known fact that the Nb-Al intermetallic alloy under study has a melting point of 2,000°C but no other details are understood as yet.

First, in configuration and properties study, the chemical configurations that did not generate cracks during solidification were identified—Nb-17.5at%Al

and Nb-Al with 4 percent of Mo, Ta, W, Co, Ni, and Si, respectively. Configurations of cast materials with Mo, Hf, and Ta additives were observed and all of them were found to contain dendrite which was destroyed when the alloy was heated to 1,800°C/4 h. This is because the alloy's configuration was made more homogeneous by heating. Commercially marketed Nb₃Al powder achieved 96 percent true density when annealed at 1,700°C by the powdered metal annealing method. Nb₃Al oxidation began at about 400°C.

In material design studies, an X-ray analysis device was developed to generate ultrahigh-temperature state charts so that test materials can be directly observed up to 2,000°C. Phase changes in Nb-Al intermetallic alloy were observed. Nb₃Al was generated as a result of crystal enveloping reaction between Nb and its liquid phase. Its existence was predicted to be around Nb-22at%Al on the high Nb side of the chemical weight composition ratio. High temperature hardening of Nb₃Al and Nb₃Al + Nb₂Al was measured by the plasma arc fusion method. Both were found to retain their values at room temperature when heated up to about 900°C. On the other hand, their values drop drastically when temperatures soar above 1,000°C thereby creating a need for ways to improve their mechanical properties at high temperature.

Dissolution and casting methods were studied as part of precision casting methods. The high melting point of Nb-Al intermetallic alloy and large difference between the individual melting points and specific weight Nb and Al created problems in its smelting process. Various studies have identified the superiority of the inductive scull melting (ISM) method employed like a melt furnace for casting. The ISM method was thus developed and homogeneous Nb₃Al with low configuration defects was successfully smelted. The material of the cast mold should not react with the melt liquid and dimensioning must also be good. High density graphite, calcia-alumina and zirconia-alumina produced good results. The chemical composition of the alloy for casting was around Nb-20at%Al and depending on small changes in its weight, the ease of casting, microstructure and room temperature characteristics differ drastically. This emphasizes the importance of chemical composition control of the alloy during dissolution.

Studies on powdered alloy fabrication methods began with thin sheet fabrication techniques using the ultrafine powder fabrication method and powder direct rolling method. The high purity melting method and powder fabrication method were studied as part of the development of ultrafine powder fabrication method. Plasma melting method was employed as a result of its cleanliness and ease of heat control. For this, a compact, pressurized plasma melting device was developed so that Al evaporation is minimum when the Ar gas pressure is 0.25 MPa. A gas atomizer was attached to this plasma melting device for fabrication of rapidly cooled solid powders. Spherical powders of average grain diameter of 120-130 μm and of high purity was successfully fabricated. In order to ensure that sintering can be performed at low temperature in the powder direct rolling method, mechanical alloying was used to create strain in the powder and to successfully lower the sintering temperature to below 350°C. The conducting powder directly rolled molding device was developed for fabricating thin sheets. The model material used was copper alloy powder. Basic molding conditions for the green sheet and the fabrication conditions for thin sheets were identified.

R&D in C/C Composite Materials

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[Article by Ryuichi Hayashi, director, Composition Performance Department,
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[Text] 1. Introduction

Space and aeronautic projects like the space plane (propelled by engines that intake air when flying in the earth's atmosphere and by rocket engines when in space), SST/HST (ultra/hypersonic transport vehicle) and methane fuel aircraft and new energy projects like coal gas power generation and nuclear fusion will take us into the 21st century. The development of new structural materials with properties like heat resistance, abrasion resistance, impact resistance, oxidation resistance, high specific strength, and high rigidity—properties that existing materials do not have that can be employed under adverse environments like ultrahigh-temperatures will be crucial to the realization of the aforementioned projects. Structures in space planes, gas turbine blades and walls of nuclear fusion reactors in particular are exposed to extremely high temperatures of 1,000~2,000°C. These materials must be reliable and able to endure adverse conditions.

In the "ultra environment-resistant advanced material" project, advanced structural materials like intermetallic compounds (IMC), carbon fiber/carbon substrate (C/C) composite material and fiber-reinforced intermetallic compound composite material were selected for study. Results of this project in its third year for the two latter materials are described below. Detailed results are described in references 1 and 2. The heat resistance at 2,000°C and the high specific strength under high temperatures and the tolerance towards matrix defects and impacts in C/C composite material are promising. Reinforced IMC composite material exhibited similar properties when employed as structural material at around 1,100°C.

2. Project Planning

This project was outsourced from six national research institutes affiliated with the Agency of Industrial Science and Technology of the Science and Technology Agency, and the New Energy Development Organization (NEDO) to nine

private corporations that are members of the Jisedai association and eight laboratories attached to PEC. Fundamental common technologies were developed by four national universities. Laboratories responsible for each study are listed below.

- Development of basic technologies for improving performance of C/C composite material (Kyushu Kogyo Gijutsu Shikenjo)
- Development of coal pitch base and polyacrylonitrile (PAN) base carbon fiber/carbon substrate composite material (Nippon Steel, Kobe Steel, and Fuji Heavy Industries)
- Development of petroleum pitch base tantalum structured carbon fiber/carbon substrate composite material (PEC Kajima Laboratory (Petoka), PEC Kawagoe Laboratory (Nissan Motors))
- Development of petroleum pitch base tantalum structured carbon fiber/carbon substrate composite material (PEC Yokohama Laboratory (Nihon Sekiyu), PEC Nagoya Laboratory (Mitsubishi Heavy Industries, Ltd.), PEC Gifu Laboratories (Kawasaki Heavy Industries, Ltd.))
- Development of petroleum pitch-base tantalum structured carbon fiber/carbon substrate composite material (PEC Oi Laboratory (Tonen), PEC Toyosu Laboratory (IHI))
- Development of fiber-reinforced TiAl base intermetallic composite material by gas method (Product Service Laboratory)
- Development of intermetallic composite material (Nihon Carbon, Ube Kosan, Mitsubishi Heavy Industries, Ltd.)

This eight-year project was split into two phases: Phase One is from FY 1989-1992 while Phase Two is from FY1993-1996. Phase One will study the basic conjugation and molding techniques for C/C composite material and fiber-reinforced intermetallic composite material while Phase Two will apply the results of the previous phase to improve the heat-resistant fiber for establishing conjugation and molding techniques.

The results at the end of Phase One of this project will contribute to basic technologies in structural materials for SST and HOPE rocket (recyclable space vehicle currently being developed to the National Space Development Agency (NASDA)—similar to the European HERMES project. By the end of Phase Two, basic technologies in ultra environment-resistant advanced materials for use in space planes and HST will be available.

3. Results on Studies on C/C Composite Material

C/C composite material is carbonified matrix reinforced by carbon fiber. New matrix and ways to produce high yield matrix must first be developed before the high-performance material can be available. Improvement of its oxidation resistance is crucial to its operating temperature. This was achieved through

studies on techniques to coat the reinforcing fiber with an oxidation-resistant layer, affinity layers between matrixes and heat-stress neutralizing layers, development of carbon dispersion prevention technology during high temperature and techniques to cover the whole composite material with a multilayer of heat-resistant composite material. New technologies must also be developed for conjugation and molding, for example, the molding method for homogeneously soaking carbon matrix in fiber to a high density and the development of new processes for yielding high-residual carbon.

Development of basic technologies for high-performance C/C composite material included simple production methods, properties measurement techniques and new oxidizing agents to improve mechanical characteristics and oxidation resistance. Bending tests of conjugated and molded two-dimensional PAN base high strength carbon fiber by the Resinger method confirmed that strength against shear strain is important. According to Fitzer,³ this is because of the difficulty in optimization in the tensile strength and shear strain with other strengths. Addition of a third component to a mixture of Mo_2B_5 and ZrB_2 is a promising oxidizing agent.

Phase One in C/C composite material development was developed into four types of carbon fiber (CF). Results obtained to date are described below.

- Coal pitch base and PAN base CF—studied conjugation, molding and oxidation prevention methods for each type of CF

(1) Studied effects of adherence between fiber and matrix and matrix packing on C/C strength. Tensile strength increased with adherence suppression. Bending strength decreased while C/C strength after treatment with graphite increased with packing.

(2) Bending strength of C/C material at $1,400^\circ\text{C}$ was higher than that at room temperature. Coefficient of thermal expansion also increased with temperature.

(3) Oxidation resistance increased with parallel use of dispersion reaction method, SiC and crack seal coating by the chemical vapor deposition (CVD) method.

- C/C composite material using petroleum pitch talandum structured CF

Studied random structured cross section of fiber, improvement of fracture distortion in matrix pitch, internal defect suppression techniques during conjugation, and improvement of oxidation resistance.

(1) The random structure is due to the configuration of the spinning jet.

(2) Selection process for easily soaked pitch that produces high-residual carbon yield is now almost complete.

(3) Minute graphite particles are fixed with pitch during carbonification to reduce the size of matrix carbon configuration. Good results were confirmed.

(4) Oxidation resistance increased with multilayer coating similar to the coal pitch system.

- C/C composite material using petroleum pitch base onion structured CF

Studied onion structure of fiber cross section, surface coating methods for CF, matrix development, conjugation and molding methods and techniques to apply oxidation resistant coats.

(1) The lower the viscosity of the yarn, the more distorted or multi angled the cross section of the fiber becomes. SiC coating of the fiber improved oxidation resistance.

(2) Matrix assumes mosaic structure with a mixture of anisotropic and isotropic layers when a mixture of phenol resin and pitch was carbonified under pressure.

(3) SiC matrix was precipitated inside porous C/C preform by the pulse chemical vapor infiltration (CVI) method. Its packing was confirmed.

(4) It was confirmed to be stabler with better thermal conductivities than Hf or Zr carbonates.

- C/C composite material using petroleum pitch base double structured CF

Studied coating techniques for CF surfaces, improvement of material performance, conjugation and molding techniques and techniques to apply oxidation resistance coats.

(1) Oxidation resistance properties of pitch base is superior to PAN base.

(2) Basic conditions for various C/C production processes like temperature gradient CVI method and composite rod method were identified.

4. Results of Studies on Fiber-Reinforced Intermetallic Composite Materials

The matrix of IMC itself is difficult to mold and as a result the development of the near-net shape molding method is crucial. Thus, in the conjugation and molding process, preform (preliminary molding material) production methods and its molding methods must be developed. Control of boundary reactions between fiber and matrix, the basic constituents in a composite material and the compatibility of these materials must be clarified. As a result, boundary issues like the effects of mutual interactions between the various constituent materials, fiber surface treatment methods, and the search for coating elements must be carefully studied.

This project will study the development of SiC fiber-reinforced IMC composite material and of IMC composite material by the gas phase method. The relatively well-studied TiAl was selected as the IMC matrix. Tensile strength of the former unidirectional material at 1,100°C was targeted for 1.2 GPa while reinforcing SiC fiber will retain its heat resistance at 1,500°C at room temperature. The establishment of basic techniques for molding IMC composite material by the gas phase method is a target in this project. Results are as below.

To obtain heat-resistant fiber-reinforced, high-performance SiC fiber must first be developed. In other words, in the conventional method, organic silicon polymer is melted and used as preform, nonfusion treated, and then spun into SiC fibers. The nonfusion treatment method by oxygen was replaced by electron beam irradiation. Oxygen content in the fiber reduced from 12 wt% to less than 3 wt% thus contributing significantly to the fiber's heat resistance and oxidation resistance.

Preliminary studies on conjugation technologies have succeeded in the production of extruded preform as the intermediate material. To control boundary reactions between fiber and matrix metal, various types of barrier materials were studied and Hf was identified as promising.

TiAl layer was successfully grown on fiber by the gas phase method where Ti and Al are successively precipitated and then heat treated.

5. Future Issues

The fracture mechanism of material under adverse conditions like ultrahigh temperature is more complicated than that at normal temperature. Ultraheat-resistant materials are used under conditions which are endlessly changing and as a result, its properties must be evaluated over a wide range of conditions. There are almost no evaluation methods for materials under high temperatures, and the development of such evaluation techniques itself will be crucial. This includes the development of techniques to measure temperature, thermal conductivity, and coefficient of thermal expansion. Results are published in references 1 and 2.

The development of C/C and fiber-reinforced intermetallic composite material will approach its mid-term assessment in FY 1992. Development of techniques that match strength characteristics of C/C composite material, implementation of this technique to the 2.5 D fiber that is popular in Europe and the United States, and then the development of new heat-resistant coating techniques will be crucial in the development of C/C composite materials. In the case of IMC composite materials, heat resistance of the heat-resistant fiber and control of boundary reactions and affinity must also be studied.

Heat resistance and strength properties of materials must be improved. Optimum testing and evaluation techniques must also be considered before they can be actually applied to real materials.

6. Conclusion

In general, material development will generate a new industry. Historically, it takes a long time. Development of ultra environment-resistant advanced material is also not an easy task. International exchanges are also important. Fortunately, symposiums on advanced composite material research are held annually. The results of this project are also presented at annual symposiums. In the future, these international presentations will be tracked while exchanges with other laboratories will be promoted.

The results of this project will be applied to the field of space, aeronautics, power generation, nuclear fusion, and other sectors of industry.

References

1. Jisedai Association, First Ultra Environment Resistant Advanced Material Symposium, October 1990.
2. Jisedai Association, Second Ultra Environment Resistant Advanced Material Symposium, October 1990.
3. Fizter, E., CARBON, Vol 25 No 2, 1987, p 163.

Results of Final Biotechnology Research Theme

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pp 111-123

[Article by Hidemasa Maeda, director, Cell Functions Department, Fermentation Research Institute]

[Text] 1. Introduction

The Agency of Industrial Science and Technology under the Ministry of International Trade and Industry (MITI) established the R&D Project of Basic Technologies for Future Industries (Jisedai Project) in 1981 for identifying future key fundamental technologies for Japan. This epochal project was established to prepare Japan for the 1990s. The main research theme will be all fundamental technologies lasting a period of about 10 years. It will be a joint effort between industrial, academic and government sectors. At the time of its establishment, this project was divided into three main themes—new performance devices, new materials and biotechnology. At that time (after the second oil shock), it was hoped that the field of biotechnology would be able to develop processes for conserving energy/resources and new biotechnologies for gene rearrangement methods developed in 1975. As a result, the field of biotechnology was divided into "bioreactors," "mass cell culture technology," and "DNA rearrangement technology" and they will last eight, nine, or ten years, respectively. The history behind the establishment of each project, research system, results and evaluation of the results are described below.

2. Bioreactor

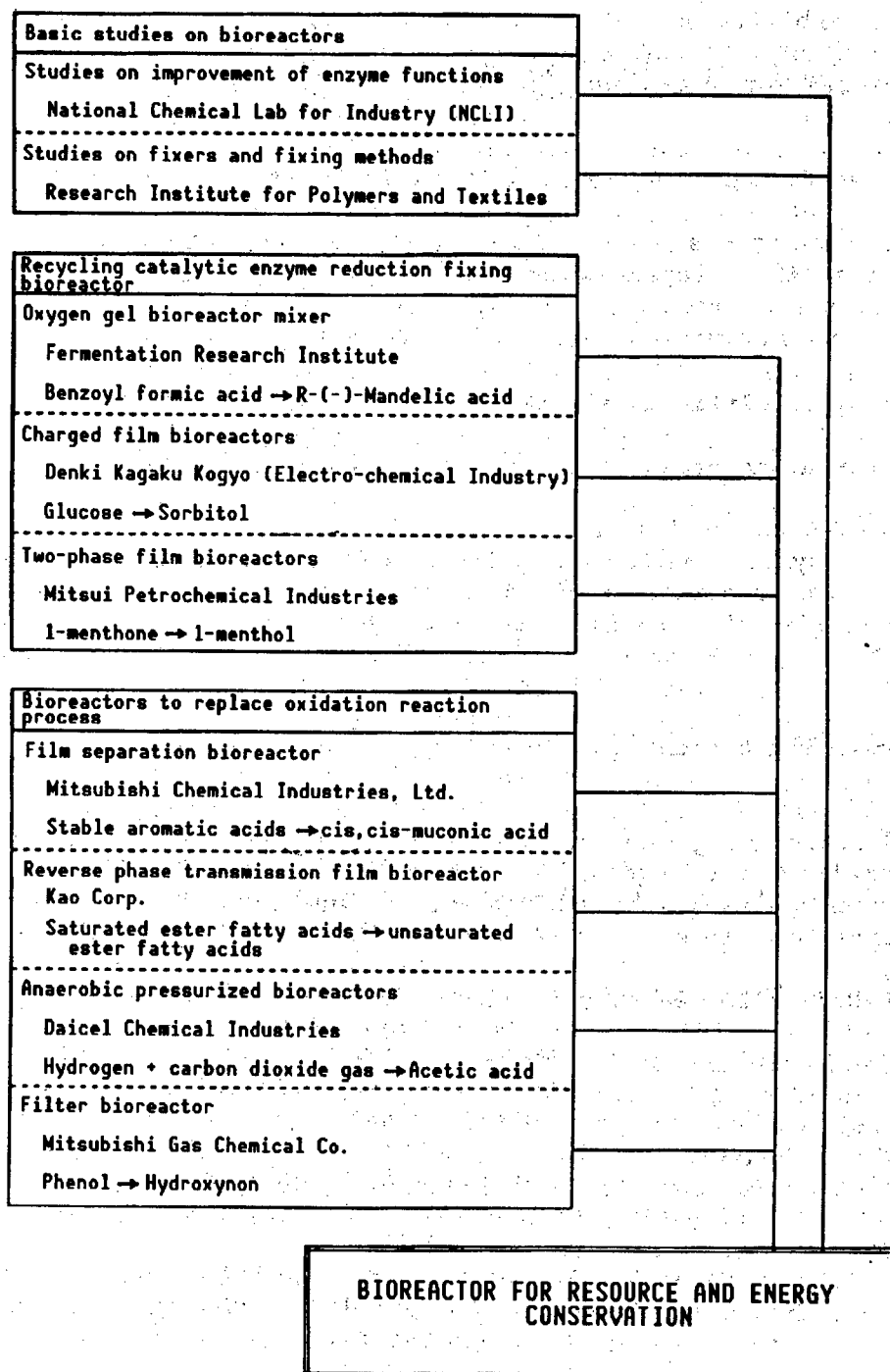
2.1 History Behind Project Establishment

Bioreactor technology which until recently was only for fine chemical products is now applied to the mass production of commodity chemical products. This is closely related to the sharp increase in crude oil prices in the late 1970s and early 1980s and bioreactor technology will help conserve resources and energy in the chemical industrial processes and at the same time, allow us to escape from our petroleum dependence.

Besides the original purpose of mass producing commodity chemicals by bioreactors, this project was also applied to the oxidation and reduction reactions that require large amounts of energy and are extremely difficult to make into bioreactors. In the oxidation reaction, numerous new technologies like oxygen supply systems that do not hamper the reaction, must be developed

while in the reduction reaction, development of effective methods to use catalytic enzymes like NAD and NADP that contribute to the biochemical reduction process, and ways to fix the whole reactive system including NAD and NADP recycled systems, will be major issues. This project therefore aims at finding solutions to these issues.

2.2 R&D System



2.3 Results of R&D

2.3.1 Fixer and fixing methods (Research Institute for Polymers and Textiles)

Studies were made selectively on polyvinyl (PVA) base fibers and photosensitive polymers by immobilization methods including the ion adsorption method and the entrapment method. Control of the micro environment around the catalyst was stressed in view of its active contribution to the fixer's biocatalyst. Stability of the fixer catalyst was also studied by making thermal measurements. These basic findings were compiled and used to trial produce a bioreactor which was continuously operated as a fixing carrier evaluating device.

2.3.2 Enzyme performance improvement (National Chemical Lab for Industry)

Nonhomogeneous reactions like catalytic reactions in organic solvents were studied. Lipase was employed as the catalyst for studying exchange reactions between tributylene and various alcohols or esters in various organic solvents. Their reactivities were confirmed.

2.3.3 Recycling catalytic enzyme reduction fixing bioreactor

2.3.3.1 Gel fixing methods (Fermentation Research Institute)

A method to envelope and fix the main reacting enzymes and that for recycling the catalytic enzymes simultaneously inside the gel was developed. Compared to model reactors, this new method allows stabler fixation of the enzymes. This method has achieved the level whereby the epochal reactor for production of photoactivated compound called R-(-)-Mandelic acid can be marketed as a total system.

2.3.3.2 Charge film bioreactor (Denki Kagaku Kogyo K.K.)

Sorbitol produced film reactor using charged filter films for effectively retaining and retrieving, within the reactive system, catalytic enzyme NAD(P) by static repulsion was developed. In this manner, a fundamental method was established for applying a feasible and multifunctional bioreactor to simple and most enzyme reactions.

2.3.3.3 Two-phase film bioreactor (Mitsui Petrochemical Industries K.K.)

Introduction of a water repelling film into the water soluble substance by the exchange reaction retains the water-dissolved enzyme and catalytic enzyme within the system and thereby helps to establish a reactor system that allows separation of nonaqueous phase selectively including the water soluble substance. Continuous reduction of 1-menthone to 1-menthol was thus possible.

2.3.4 Bioreactor to replace oxidation process

2.3.4.1 Use of Ansoku kousan benzoic acid (Mitsubishi Chemical Industries, Ltd.)

A total bioreactor system for replacing the oxidation process in effective production of muconic acid from stable aromatic acids was created.

2.3.4.2 Fatty acids and oxidation of inductive fatty acids (Kao Corporation)

A reverse phase transmission bioreactor system was developed for extracting the oil phase by using film to interchange the water and oil phase. In this manner, the oxidation reaction inside the molecules of the saturated ester fatty acids (unsaturation) which are currently not chemically synthesized on an industrial scale, can now be realized.

2.3.4.3 Use of carbon dioxide (Daicel Chemical Industries, Ltd.)

Acetic acid was produced from carbon dioxide gas and hydrogen by a reactor system using partially anaerobic bacterial film filter—a system that is relatively unknown and requires highly advanced anaerobic techniques. In this manner, fundamental technology related to industrial applications of strict anaerobic bacteria was established.

2.3.4.4 Hydroxynon production (Mitsubishi Gas Chemical Co., Inc.)

A highly-feasible bioreactor system for producing hydroxynon from phenol was created.

2.4 Evaluation of R&D

This project has confirmed that through the creation of various bioreactor model systems and verification of their operations, they can be applied to new chemical reactive processes which were previously believed impossible. Sub-themes in each bioreactor system have greatly expanded the possibilities of bioreactor technology through the creation and verified operation of model systems applied to commodity chemicals or to oxidation or reduction processes which are highly advanced and extremely difficult targets. In this sense, these themes have produced extremely meaningful results.

This research and development project has contributed greatly to the next-generation bioreactor technology and has helped it achieve its final target.

The following issues still remain. In this project, film reactor development and fixing methods were studied as methods to create bioreactors. New film reactors were developed from charged films and water repellant films. This technology should be highly acclaimed as reactor technology. In the development of new fixing methods, the oxidizing and reducing systems were not selected because of difficulties in the oxygen supply to the oxidizing reactor system and cost problems in polymerization of the catalytic enzyme in the reducing reactor system. Although this method is attractive from the point of durability, its development should be to overcome the aforementioned shortcomings.

Besides its direct contribution to the creation of bioreactor model systems, this project also produced screening results. About 30,000 stocks of bacteria were screened for application in actual bioreactor systems. Various useful light activated organic manufactured microorganisms and enzymes are already available through this screening process although they are not included in the system. They can be employed in actual bioreactors. The availability of

numerous microorganisms with various properties will definitely contribute to future bioprocesses although they are not expected to be employed in reactors. This confirms the importance of the screening process in biotechnology. It is not an exaggeration to say that the numerous microorganisms separated by screening is a major breakthrough for this project.

Effective joint studies on bioreactors to replace reduction reactions were successful because of the smooth technology transfer from the national research laboratories to private corporations. This was achieved in Phase One by sending two delegate researchers from the private corporations to work at the national research laboratories where research on bioreactors for enzyme and coenzyme had been under way even prior to this project. The cooperative system continued even after the project transferred to private corporations.

Phases One and Two of this entire project had a total of 34 papers published in international journals, 12 international patents pending, and 151 domestic patents pending. The results of this project were compiled and published in the international journal, J. BIOTECHNOLOGY. Of the patents applied, production of R-(-)-Mandelic acid for industrial use is attracting a lot of attention and most of the papers presented are also attracting a lot of interest both internationally and domestically. Verbal presentations were also frequently made at international symposia. These efforts to advertise the results of this project are also well received.

3. Cell Mass Culture Technology

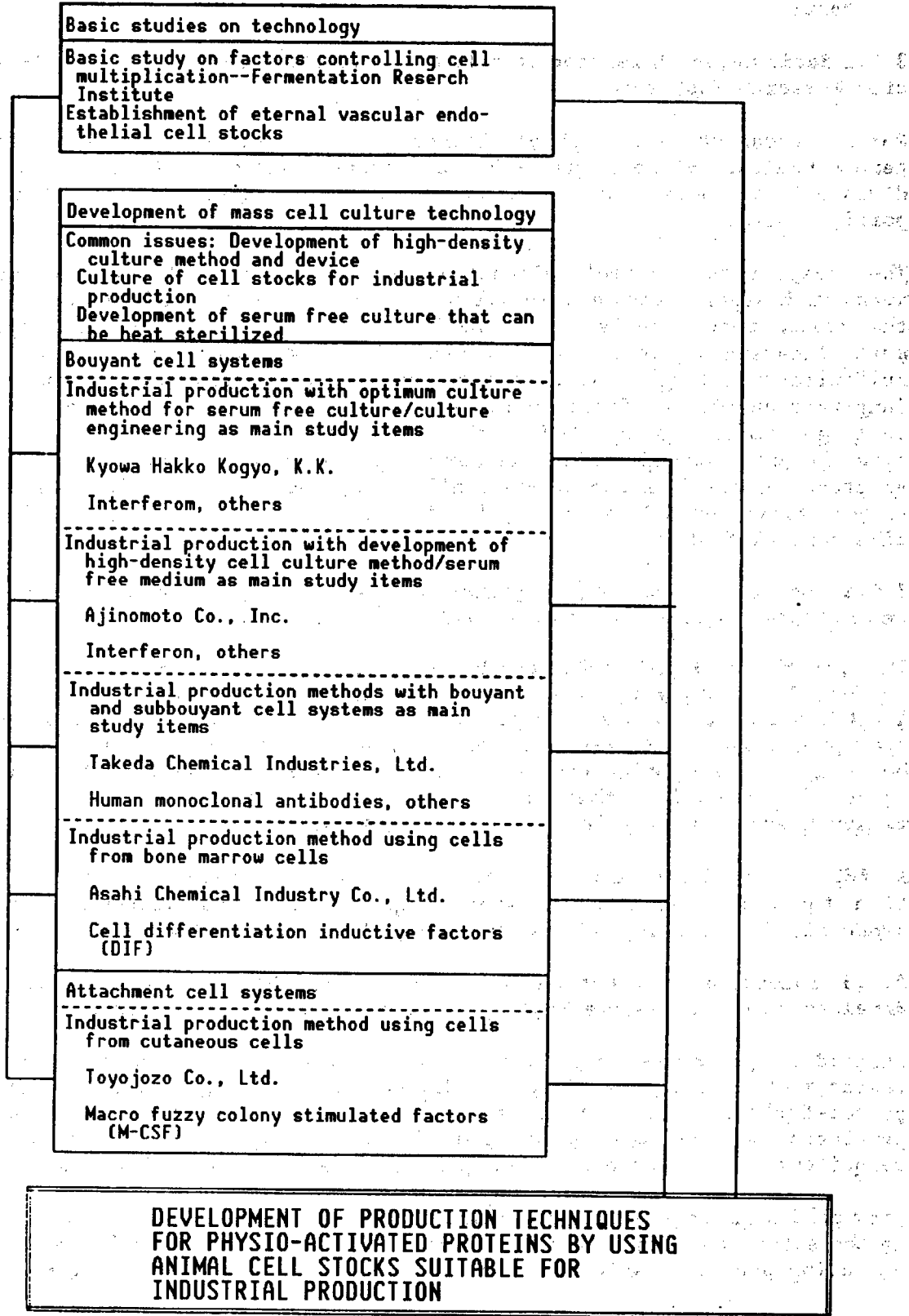
3.1 History Behind Development of Project

Culture of cells from higher animals in a liquid culture medium progressed rapidly in the late 1970s and early 1980s. Great hope was placed on the possible industrial production of various physiology activating proteins like interferons from animal cell cultures and monoclonal antibodies that require antiviral activation. However, animal cells multiply at a rate that is very much slower than normal microorganisms. Development of a large-scale culture system is crucial since production weight per cell is also very low.

Major technical issues identified at that time--in cell mass culture on an industrial scale--are:

- (1) The search for cells that allow production of the useful substance targeted.
- (2) Reduction of the amount of fetal serum required for cell culture by replacing the various cell multiplication factors or acclimatizing the cells. This is because the bovine fetal serum required for growing most of the animal cells is very costly and the quality is inconsistent. A final solution would be to perform cell culture in a serum free medium. the development of identification culture media that can be widely applied and sterilized by heating.
- (3) To improve productivity, techniques for culturing high-cell density and effective refinement of the products must be developed.

3.2 R&D System



3.3 Results

3.3.1 Basic research related to cell multiplication control factors (Fermentation Research Institute)

Normal permanent cell stock of chromosome number was established after long-term subculture of more than 250 DPLs (average number of times of cell group division) was made from the endothelial cells taken from normal cells in porcine aorta.

The acceptor for the multiplication control factor bFGF was produced. bFGF works with heparin and heparin sulfuric acid on vascular endothelial cells and the smooth muscle cells of the bFGF acceptor. This is the first time cell multiplication control was observed. The vital continuous effect of the multiplication factor (aFGF) and multiplication control factor (heparin) in long-term culture of finite multiplication cells is a new discovery. Success in long-term culture has led to the discovery of endoserine, a vasoconstrictive factor, through joint research efforts with Tsukuba University. The existence of family sequence was confirmed through determination of structures of homologous genes in heparin sulfuric acid proteoglycan (HSPG), a multiplication control factor.

3.2.2 Industrial production methods by optimal culture of serum free medium and culture engineering as main methods (Kyowa Hakko Kogyo K.K.)

The growth of KJM-1 cell stocks in serum free medium was successfully performed by nurturing namalwa cells. High productivity of α -interferon at 100,000 units per ml was recorded with this cell stock. It was also confirmed that production of β , γ -interferon, lymphotoxin and G-CSF is possible by the heterogene introduction method. This cell stock is a gene host with a wide range of applications that allow buoyant culture growth in human serum free medium thereby proving its worth in industrial use.

An 18L size device made up of a culture perfusion device with cell precipitation tube, silicon module enzyme supply device and dialysis device was produced. Cell density of 5×10^7 cells/ml was obtained with this device.

3.3.3 Industrial production method with high-density culture method and development of serum-free medium as the main study item (Ajinomoto Co., Inc.)

Instead of glutamine that is a vital nutrient for various types of cells, replacement substances like oxidation-resistant glutamine peptide was successfully developed. Replacements for albumin and transferrin were also developed. All components of these serum-free cultures are buoyant, have ubiquitous attachment properties and can be sterilized by heating.

The world's maximum $1\sim 2 \times 10^8$ cells/ml were successfully maintained for 80 days in the serum-free human lymph cells in the dialysis device (culture 1L, medium 5L) using porous ceramics carrier. High productivity was confirmed.

3.3.4 Industrial production method with buoyant and subbouyant cell systems (Takeda Chemical Industries, Ltd.)

Anti-tetanus toxoid monoclonal antibodies producing cell stock and anti-B hepatitis virus surface antigen human monoclonal antibodies producing cell stock was produced. The latter produces neutralizing antibodies in chimpanzees. This effect was confirmed for the first time in the world. Breeding was done by nurturing in a non-protein medium and recloning, culturing cells generated by human interleukin 2 acceptor gene introduction in a medium that contains human interleukin 2, or by re-cell fusion of hybridoma homologous. This has significantly improved productivity of the antibodies to 327 mg/L/day (10 ml). In the culture of human-human hybridoma, GFS that contains cell multiplication factors of cheap mature bovine serum was extracted. The synthesized polyethylene glycol was found to promote cell multiplication. A serum-free medium was developed from this.

3.3.5 Industrial production method using marrow cells (Asahi Chemical Industry Co., Ltd.)

A cell stock bred on a serum-free medium was obtained from highly-productive DIF (cell differentiation inductive factor) stock taken from THP-1 marrow cell stock. This stock was induced to differentiate into cells that produce DIF from undifferentiated cells. In this manner, a basic technique was developed with reference to new culture techniques that classify the production sequences of the target substance in the same manner as cell multiplication. DIF productivity was 800 units/ml. DIF discovered in this project is a new physio-activating substance. It is also a multifunctional substance that induces differentiation of the erythroblast and spherical colonies in the undifferentiated marrow cells.

Techniques were developed to produce DIF. Production of TNF was also confirmed to be important.

3.3.6 Industrial production method using cells taken from cutaneous cells (Toyojozo Co., Ltd.)

The cutaneous cell stock TRC-29SF was established from the colony stimulating factor (M-CSF) produced in human gastric cancer. The M-CSF gene was cloned from this and retransferred to TRC-29SF to increase expression. This new breeding method will find wide applications as a method to increase secretion by removing the hydrophobic part of the gene. Effective and superior adhering methods were developed for micro carrier particles and the world's best result of 1.2×10^7 cells/ml was recorded through improvements in the culture medium.

Substances that exhibit the multiplication effect due to blood were confirmed with these cells. These substances can be replaced by retinoid to allow industrial production of serum-free medium.

3.4 Evaluation of R&D Results

Useful cells were selected and bred in this project. Stocks that effectively produced useful proteins like interferon and differentiation inductive

factors, serum-free medium stock for nurturing, general-purpose host cell stock for gene introduction, human-human hybridoma stock and eternal vascular endothelial cell stock were established. This has enabled large-scale production of DIF which, until then could only be produced in small amounts. Identification of its functions will create new applications in the field of medicine. The production of human monoclonal antibodies for anti-HB virus activation is also possible now. This antibody is more active than conventional polyclonal antibodies and was confirmed to be effective against B-hepatitis virus in chimpanzee experiments.

A serum-free medium that can be sterilized by heating and can be widely applied was also successfully developed. Culture cost thus dropped to about less than one-tenth of normal costs. Supply of culture medium as a constant quality is now possible.

Development of the culture perfusion device with cell precipitation tube attached and application techniques for various other perfusion culture devices improved culture capability in a buoyant system to 2×10^8 cells/ml irrespective of whether in a serum-free medium or not. This is a significant record since the world's record to date is only 2×10^8 cells/ml. Cell growth in adhesive cutaneous cells in a serum-free medium by the macro carrier culture method, is also a world standard of 1.2×10^7 cells/ml.

This project (Phases One through Three) has a total of 45 publications in international journals, eight international patents pending, and 70 domestic patents pending. Verbal presentations at both international and domestic symposia were also numerous. An annual symposium was also organized to announce results of this project while all results were compiled and published in the journal, CYTOTECHNOLOGY.

A serum-free culture medium and high-density culture techniques are expected to find wide applications in industrial production of substances from animal cells. Studies on physiological functions of DIF are expected to become more active in the future.

4. Technologies To Use Recombinant DNA

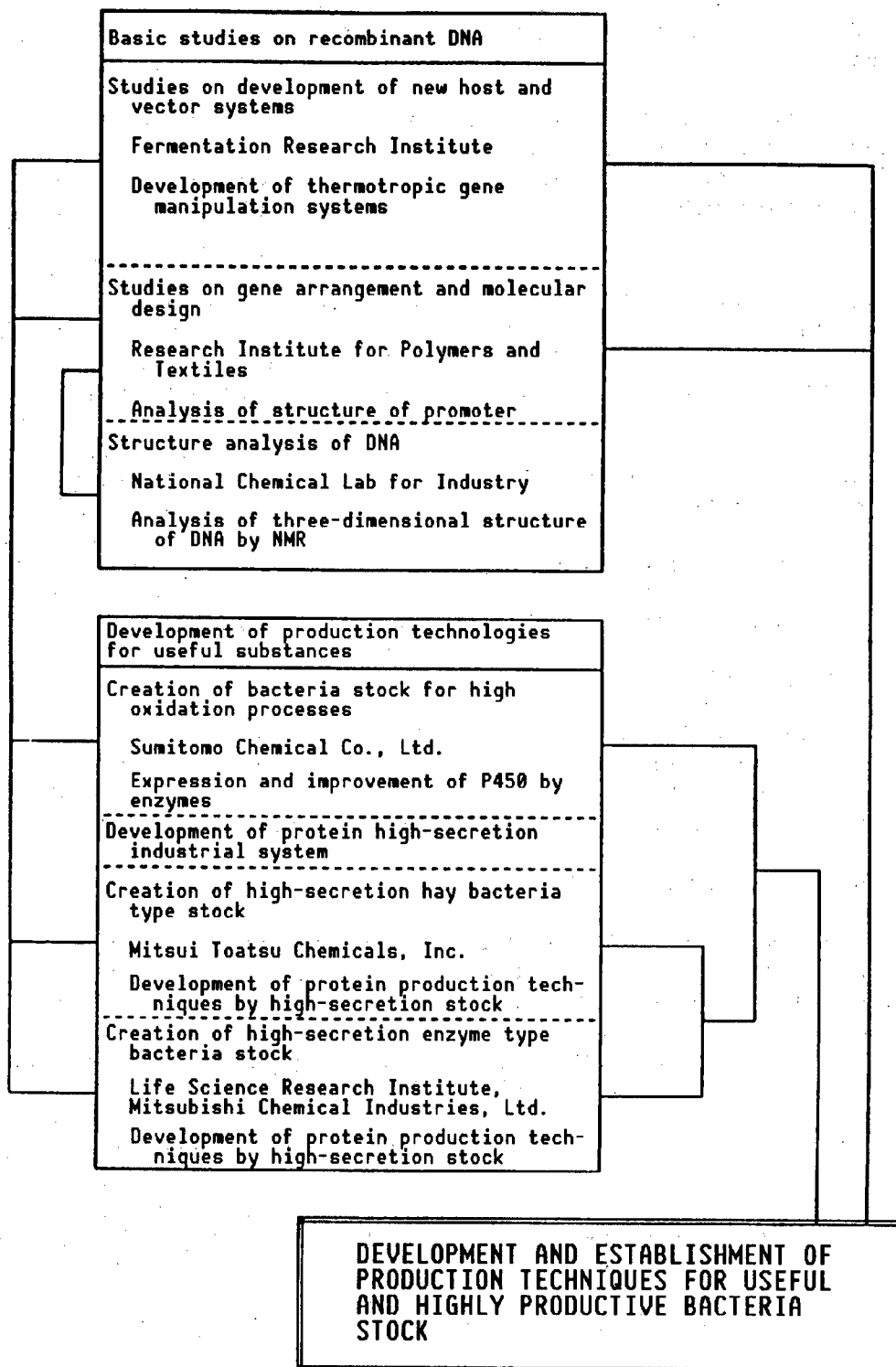
4.1 History Behind Establishment of Project

The DNA manipulation technology was already widespread in the early 1980s when this project was established. At that time, the introduction and expression of genes in a different species of organism was already possible. This project aims at large quantity artificial expression of genes taken from higher animals onto microorganisms and the development of DNA manipulation technologies on an industrial scale.

Japan has reconfirmed from experiences during the two oil shocks that it is vital for her to eliminate her dependence on oil in her chemical industries. Development of recombinant DNA technology which is the key technology for future bioindustries will be actively pursued by joint efforts between the industrial, academic and government sectors. Recombinant DNA technology is also quite advanced in Europe and the United States and related patents are

numerous. it is thus crucial for Japan to develop her own recombinant DNA techniques for her micro and chemical industries.

4.2 Research System



4.3 Results

4.3.1 Basic recombinant DNA technologies

4.3.1.1 Studies on development of new host and vector systems (Fermentation Research Institute)

The *Thermus thermophilus* HB27 stock was selected as an advanced thermotropic bacteria host. Numerous new cryptic plasmid were separated and of these pTT8 was bonded to β -galactosidase gene to generate a transformant which created the color distinguishable vector colony on a gelatin culture medium that contains Xgal.

Tryptofan synthesized enzyme gene was cloned from HB27 stock and the base configuration was determined. Tryptofan synthesized enzyme gene was bonded to *Thermus* T2 stock to produce pTT8 plasmid. The variant of the tryptofan synthesized enzyme gene host generated the complementary plasmid vector pYK109.

4.3.1.2 Studies on gene configuration and molecule design (Research Institute for Polymers and Textiles)

Plasmid vectors for cloning promoter and terminator were created and their activities measured. Of the chemically synthesized promoters, the consensus configuration that recognizes σ^{70} type RNA polymerase exhibited highly activated strength. ρ factor nondependent configuration was synthesized with terminator configuration and its transcribed release activity was measured.

Target gene product separation by protein dissociation enzyme was prevented by expressing the target gene product as a fused protein with DHFR. This method helped ease separation of the target gene product by storing fused protein of up to 20 percent of the total protein within the myocyte.

4.3.1.3 Structure analysis of DNA (National Chemical Lab for Industry)

The FAB method was employed for analyzing trace amounts (several hundred μg) of synthesized and extracted DNA. From this, a method to determine the base configuration of the previously difficult to observe 7-nucleotide DNA was developed and successfully applied to the "TATA" box promoter DNA model. Structure analysis of the chemically synthesized promoter DNA fragments and other synthesized DNA were performed by NMR.

4.3.2 Production of bacteria stock for high oxidation processes (Sumitomo Chemical Co., Ltd.)

Recombinant yeast stock was used to produce fused enzymes from bovine adrenal microsome type P450c₁₇ and yeast reductase. About 380 mg/L/day of 17 α -hydroxyprogesterone was produced from 1g/L of progesterone. Similarly, recombinant that produces fused enzymes from bovine adrenal microsome type

P450c₂₁ and yeast reducing enzymes produced about 215 mg/L/day of 11-dioxycortisol from 1g/L of 17 α -hydroxyprogesterone. Mitochondria type P450 also produced similar results.

In these research processes, the accurate transport of p450 taken from higher animals to yeast microsome of mitochondria which are eucaryote are important for function expression. In artificially fused enzymes, this transport into the molecule is done electronically and reaction speeds have been confirmed to be very much higher than natural enzymes. P450 production inside the yeast increases by about four times when mitochondria type P450c₂₅ is transformed into microsome type. P450c₂₅ expressed on yeast microsome exhibited 1 α -hydroxy vitamin D₃ 25 hydroxyl activity that is about 50 times higher than when expressed in mitochondria.

4.3.3 Creation of hay bacteria type high-secretion host bacteria stock (Mitsui Toatsu Chemical, Inc.)

Genes related to suppression of new protease production was isolated when improving the host for PAI and its applications such that high secretion new recombinant hay bacteria stock can be generated. The structure and characteristics of this isolated gene were determined. These results were applied for the first time to improving the host that is required for the generation of high-secretion production systems. Hay bacteria host with significantly reduced protease activity was successfully generated.

The refolding method was established during culture of secretive production of improved hirudine. A concentrated medium secreted 350 mg/L/7hr, a value that is higher than normal culture. This protein secretion of gene product from high-level eucaryotic cells including other systems is a world standard.

In the case of human growth hormones, we have also attained a world record of 200 mg/L/8 hr (culture medium exchange method) of hay bacteria secretion on a flask scale. Even on a fermenter scale, similar high productivity of 80 mg/L was observed.

4.3.4 Creation of high-secretion yeast type bacteria stock (Life Science Research Institute, Mitsubishi Chemical Industries, Ltd.)

New recombinants were successfully created by establishing new vectors including invertase gene promoter and introducing them to *Saccharomyces cerevisiae*. Mouse α -amylase was used as the heterogene for confirming the high-secretive property of this recombinant. Secretion of 690 mg/L/3 days was observed in the jar culture of controlled glucose concentration. Attempts to increase secretions of various host vector systems resulted in 31.5mg/L/3days of human β -endorphin.

The secretion of activated nerve growth factor was successfully achieved for the first time in history and secretion of 1 mg/L/day was finally obtained after studies and improvements in the culture medium. After partial refinement of the secreted nerve growth factor, promising configurations were confirmed. Activity using PC12 cells was also confirmed.

New units were stabilized and multiplied by inserting new plasmid into δ configuration area in chromosomes. Secretion of 10 mg/L/day was observed.

4.4 Evaluation

The results of this project are as follows:

(1) Establishment of p450 gene expression systems taken from microsome and mitochondria and for the first time in history simultaneous expression of p450 and reductase. World leader in creation of fused enzymes from p450 and reductase and genetic bonding. This helped industrialize bioprocesses that employ recombinant yeast. This has also contributed to basic studies on molecular biology of p450. The possible application to bioprocesses of p450 mono oxygenase is widely acclaimed.

(2) Analysis of genes related to production suppression of new protease like PAI and improvement of its host through its applications was successfully generated for the first time in history for creation of high-secretion new recombinant hay bacteria stock. Hay bacteria host with significantly reduced protease activity was created. Low cost, highly productive refolding method during culture for zenoprotein was established. High secretions of improved hirudine and growth hormone was achieved and widely acclaimed.

Isolation of PAI gene and its analysis are crucial for clarifying transcriptional control and information transmission in basic biology. Studies on the molecular biology of hay bacteria is considered a breakthrough in this field.

(3) New recombinant yeast stock was generated with new vector that contains invertase gene promoter. High secretion of 690 mg/L/3 days mouse α -amylase was achieved by glucose concentration controlled jar fermenter culture. β -endorphine and human NGF secretions are also world standards thus proving the usefulness of host and vector systems.

Clarification of factor technologies that contribute to yeast expression and secretion in turn helped identify the transcription, information transmission and secretion mechanism of yeast. This is a definite contribution to basic research on a world standard.

(4) An overview of results of the research titled "basic techniques in recombinant DNA" completed in Phase Two by national laboratories is described below:

Highly effective expression vector of mid-thermotropic bacteria was created and its usefulness verified. Highly thermotropic bacteria host and vector systems were developed for the first time in history thereby allowing thermotropic bacteria to be produced on an industrial basis.

Highly effective expression of heterogene vector was successfully created from the dihydrofolic acid reductase gene. The heterogene product can be effectively produced as a byproduct of dihydrofolic acid reductase and fused protein. At the same time, effective refinement of the target protein and peptide was verified.

The sub-project, "structure analysis of DNA" ended with identification of the relationship between biological structure and functions of DNA but it has contributed to new insights into the structure of oligonucleotide.

This project carried out in three phases resulted in the publication of 69 papers in international journals, 10 international patents pending, and 141 domestic patents pending. In particular, most of the results are published in international journals and received worldwide acclaim. Annual symposia for announcing results of this project are also well received.

Trends in Biotechnology

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pp 125-130

[Article by Noboru Tomizuka, director, Function Development, Fermentation Research Institute]

[Text] 1. Introduction

The Jisedai Project is now approaching its tenth year and biotechnology is one of its key technologies. It has matured from a "dream" technology to one that has generated a whole new industry through its contribution to our knowledge on its fundamentals and applications. Biotechnology applications range from medicine, pharmaceuticals and drugs, to food and fibers and is rapidly expanding to cover fields like agriculture, forestry, fisheries, environment, resources, and energy. It will also develop a new engineering concept for the next century.

An overview of the trends in biotechnology in the past 10 years and future prospects are described below.

2. Government's Policy on Promotion of Biotechnology

Japan's biotechnology research began with full governmental support. A research consortium was established upon commencement of the Jisedai Project and numerous laboratories were commissioned to do research in biotechnology. The national budget for biotechnology-related research increased more than tenfold in the past 10 years. In FY 1992, the budget was about ¥100 billion. Numerous special departments were established in the government sector in this 10-year span. Associations of corporations that deal with biotechnology were established. Meanwhile, funding organizations for private organizations were also established. MITI established the Biochemical Industries division under the Basic Industries Bureau to manage the Bioindustry Association, which in turn established the Japan Key Technology Center, a funding body for promoting studies on biotechnology. MITI has, after launching the Jisedai Project in 1981, announced new themes like the water recycling system (1985), protein engineering (1986), plant cell biotechnology (1986), ocean biotechnology (1988), and earth environment (1990). Restructuring of national research

organizations and laboratories was implemented after establishment of the HSFP organization.

The government's budget for biotechnology-related research is estimated to be less than half that from private corporations. R&D of products was done solely by private corporations. The government's pioneering role as a leader in this project for private corporations is shifting to one that emphasizes international contribution and technological innovation which currently lacks industrial advantage yet requires large capital outlay. It is also shifting to basic research that involves the general public including resources, energy, earth environment, and public safety sectors. For example, the key to discovering the whole DNA configuration for a particular living organism will depend on the development of effective analytical and information processing techniques.

3. Recombinant DNA Experiments and Public Acceptance

3.1 Experiment Guidelines and Industrial Application Guidelines

Consideration of the dangers of the unknown in recombinant DNA was done for more than 15 years and this was presented at the Ashiloma (phonetic) Conference. This is the major difference with other advanced technologies.

The Japanese Ministry of Education released a set of research guidelines on recombinant DNA to universities on 29 March 1979. The Science and Technology Agency then issued another set of guidelines in August of the same year to private corporations and national research institutes. Both sets of guidelines focused on artificial recombination of parts of the DNA in living organisms. The caution towards recombinant DNA technology gradually subsidized after numerous tests proved their irrelevance. The guidelines were revised and the strict rules and regulations on such research gradually relaxed thus triggering an increase in the number of studies. In the revision in 1991, some experiments could be pursued under the researchers' own discretion. Although Japan began recombination experiments on plants at isolated experimental stations in 1991, other nations have already performed several hundred outdoor experiments on living animals and microorganisms. This proves that Japan is lagging behind other nations and this is becoming a major issue.

It has been five years since MITI's "Recombinant DNA Engineering Guideline" based on the 1986 OECD Council's advice was announced in June 1981. Since then, the Ministry of Health and Welfare and the Ministry of Agriculture, Forestry and Fisheries have also issued similar guidelines. Industrial application guidelines were based on evaluation of the host safety. Good industrial production standards (GILSP) was introduced to ensure that non-disease causing recombinant DNA with low survival and breeding capabilities are not released into the environment. As a result, normal industrial facilities more than suffice for the GILSP recombinant. Based on the industrial application guidelines from each ministry, about 300 industrialization projects were confirmed at the end of 1991. Safety evaluations of large-scale outdoor experiments, however, were still performed on a case-by-case basis depending on the product, and a step-by-step basis depending on the scale of

the experiment, by OECD biotechnology safety experts. This is expected to affect studies on recombination of DNA in outdoor animals.

3.2 Public Acceptance

There were cases in the past when Japan had to abandon her development projects because of lack of support from the general public. An example is the development of petroleum protein. Public protests and court cases against projects like P4 experiments by the Physico-Chemical Research Institute, relocation of the National Preventive Hygiene Research Institute, establishment of Japan Tobacco's research laboratory and the establishment of Osaka bioscience laboratory are some cases that are currently under debate. The dissemination of accurate information is crucial for public cooperation and acceptance while cooperation among government, private corporations, and researchers is vital to the success of these projects.

There was a large volume of biotechnology-related news everyday in the mass media when the Jisedai Project was launched but the volume has steadily dropped as the field became more complex and diversified although the strength of impact by mass media is well understood. The Bioindustry Association and some corporations have organized lectures and symposia to disseminate information on biotechnology to the public. Videos and books were also prepared. Local promotion groups were involved in activities to spread knowledge about the field. For example, the Okayama Biotechnology Panel was established to organize regular symposia with Okayama University, local organizations and Okayama prefectural government to help disseminate information on biotechnology and research results. Annual seminars and workshops were also organized for high schools. These activities and full government support are crucial.

4. Intelligent Property Copyrights and Biotechnology Patents

The mass media has news on intelligent property copyrights and patents every day. Interest is not only increasing at the private corporation level but also at the government level. The patent suit between Gentech of the United States, and Toyobo, patent application for human genome by the U.S. National Institutes of Health (NIH), and legal systems to protect new plant hybrids are some of the cases that were widely publicized. These cases became problems because of the different methods of handling in each nation, the case's relationship with international projects and the absence of domestic law to handle the situations. Research is carried out in countries yet the corporations that own the research cross borders and globalize. Joint research with groups that belong to more than one nation are currently being pursued and it does not make sense for such discoveries or inventions to be protected by laws that differ from nation to nation. A global system should be established to protect the world's properties. Both the public and the private sector must realize the importance of revising the current legal system in each nation and enact a new system based on the development of human resources.

The number of biotechnology-related patents applied for and approved has increased significantly in the past 10 years. The peak, however, has passed.

A similar trend can be observed in the field of gene recombination technology. The number of applications for patents in Japan is increasing, an indication of the maturity of the basic technology. There is a recent rise in applications for patents in basic processes in various fields, specific cell stock or seeds and DNA branch configuration. The trend is the establishment of unique and practical patents. Japan's progress in biotechnology will only be possible through revolutionary research. A result of this will be an increased number of patent applications. Therefore, Japan must shift from a quantity based patent application system to one that emphasizes quality by standardizing international efforts on the patent system for speeding up patent evaluations. An evaluation system that emphasizes patent quality must be established.

Japan has an "entrusting" system for proving completion of research on patents related to living organisms, plant and animal cells. This body goes by the name of the Fermentation Research Institute of the Agency of Industrial Science and Technology. The number of stocks stored here is over 10,000 and the percentage stored by international organizations is increasing. These patents are not recognized internationally as either animal or plant patents. Neither the patent system nor the patent evaluation system usually accompanies technological progress because regulations for microorganisms are incomplete. For example, patents are considered sold at different times depending on the nation where it was handled and at the same time, regulations on the buyer also differ depending on the nation. A standard system is thus crucial.

5. Trends in Corporations Handling Biotechnology

Biotechnology contributes to both the process and the product of processes in living organisms. Products that used cell fusion technology were the first to be marketed. Today medical drugs that use gene recombination technology, diagnostic drugs and identification enzymes are some of the products that have entered the biotechnology market. Gene recombination technology is important because of its "newness" and its impact on the market. Scientific knowledge on genetic recombination technology increases while at the same time, tools required for research become automated and human attendance is not required. Samples for experimentation becomes fewer (high sensitivity) while test drug kits are also marketed. The burden on facilities decreased with a relaxation of experimental guidelines. As a result, it is becoming relatively easier for private corporations to participate in genetic recombination technology.

The objective for corporations that deal in biotechnology are the search for solutions to issues in medical welfare, information service, earth environment, resources, energy, human population and food supply. It is apparent from the biotechnology product market that drugs are the main products. In the field of genetic recombination, there are medical drugs like erythropoietin, growth hormones, and enzymes like detergents while in the field of cell fusion technology, monoclonal antibodies outpatient drugs, and in the field of cell culture, there are interferons. Realization of genetic recombination technology is evident from the number of applications at each ministry, for recombinant DNA experiments for industrial use. Applications at MITI include substances for physiology activation, diagnostic drugs, vaccines and curative enzymes. Future biotechnology is expected to contribute to the development of

agriculture, forestry and fisheries industries that are relatively energy consuming, resources consuming and noneffective as well as to industries dealing in foodstuffs, transportation, storage, safety evaluation, fashion and trends evaluation, and environment cleansing. Therefore, the flow of knowledge, raw materials and technologies developed by R&D type of corporations to product development corporations will increase.

6. Development of Biotechnology Using Living Organisms

6.1 Technology That Uses Genetic Information

Significant progress was achieved in the three sectors in genetic recombination technology—genetic cloning, analysis of genetic structure and function, analysis of genetic structure and functions of genetic products. This has led to a significant expansion in the types of applications for genetic information. Instead of single gene operation in genetic cloning, multiple gene operation became possible. Expression cloning of genes from various living organisms became possible. The genetic expression mechanism was identified and control of an arbitrary position of a gene as well as control of activation of anti-sense technology became possible. Genetic operation of various living organisms also became possible while quantitative and qualitative expansion of the range of application to useful products like the secretion of proteins outside bacteria became a reality. In the analysis of structure and functions of genetic products study, production of natural protein (in protein engineering) shifted to the design and fabrication of artificial protein. Research in various fields are expected to progress rapidly and chromosomal level control will become a reality. This hopefully will contribute to the development of techniques for advanced application of bioreactions.

6.2 Biosubstance Application Technology

Progress ranging from genetic cloning to process techniques for protein creation will be the keys to development in various molecule engineering fields like protein engineering, glyco engineering, and RNA engineering. The nature of bio high polymers will be modified while applications of process technologies like stabilization of enzymes will expand. Design and fabrication techniques in protein engineering will shift from the general-purpose natural protein to specific (customized) artificial protein. In the future, mass production of customized protein instead of standard protein will become a reality.

Progress in studies on self-configuration structuring techniques (a characteristic of biostructures) will become the origin of concepts on complicated system designs and software designs like molecular machines or molecular factories. It will be the birth of biotechnological products. As a result, actual studies on promising biotechnological products like precisely synthesized bioreactors, highly sensitive and precise biosensors are extremely pressing. Research will progress by leaps once the objectives are set.

6.3 Techniques That Employ Breeding Capabilities

Genetic operation in living organisms will shift from colon bacillus and yeast to microorganisms for industrial application, from plant and animal cell to individual units. Each type of cell has a complicated chemical structure and creates high polymer substances. It also modifies specific parts and controls synthesis of chemical substances, and has accurate information transmission and defense capabilities as well. On the other hand, cells also have characteristics peculiar to the living organism to which they "belong." Cells in microorganisms consume substances while animal cells perform the immunity function through contributions from chemical substances. Plant cells have all functions and produce the required chemical substances through photosynthesis. Therefore, a living organism has "seeds" for the development of a wide range of technologies and products based on its diverse functions. It is crucial for a reevaluation of and search for biofunctions to meet the changes in demands and needs.

Industrial application of characteristic cells has already entered a system that is similar to existing chemical industries that accompany development of genetic operation techniques. In other words, application industries for microorganisms, animal or plant cells use high quality cells as the source by separation from the microorganism group or unit, splitting and then extraction of a single cell. It is then bred into microorganism flora, unit body or organ, produced, and then the cell quality is improved by genetic operation or cell fusion. Functions of the cells are then advanced and finally production of a useful substance is achieved through culture. In this manner, this process is similar to a chemical industrial system. Therefore, studies on control of physiological effects in various cells, cell groups or small organs, substance transformation capabilities, energy transformation capabilities and clarification of information transmission-transformation functions will become more and more important as we industrialize applications for cell breeding technology. The results will hopefully contribute to solutions to environment, resource, and energy problems. In particular, the biochemical technology that aims at the development of advanced applications of fossilized resources (which is said to be the cause of reduction of extractable fossil resources and environmental pollution) and biomass chemical industries will develop cells with modified metabolic processes or sex-resistant enzyme genes introduced. It also aims at the development of environment-friendly techniques to produce high-performance substances. Progress in metabolic engineering is crucial for the development of the metabolism of substances and production performance application techniques.

7. Conclusion

Progress in biotechnology is based on the results of research in biology, chemistry, physics, medicine, engineering and agriculture. A delay in developments in any of these fields will in turn cause a delay in developments in biotechnology. Biotechnology is not for producing independent results but instead takes on meaning when developed with other technical fields and society. It is for furthering progress in current technologies. Progress in biotechnology can only be achieved through consolidation of related and support areas.

R&D in Application Technologies for Functional Protein Aggregate

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[Article by Professor Karube, Research Center for Advanced Science and Technology, Tokyo University]

[Text] 1. Introduction

This research and development project is the fourth part of a biotechnology program (bioreactor, cell mass culture, recombinant DNA application technology) outsourced to the Biotechnology R&D Engineering Consortium from the Jisedai Association. This 10-year program began in 1989 and is now in its third year. Seven corporations, five national research institutes, five universities, and one foreign research institute are the participants in this research program.

The purpose of this project is to technically reproduce the composite functions in functional protein aggregates and to artificially create functional protein aggregates that allow controllable chemical reactions like matter production that have high selectivity, specificity or matter transformation reactions.

An overview of the R&D project and the results are described below.

2. Overview of R&D Project

2.1 Development of High-Function Molecule Aggregates by Configuration Engineering of Functional Protein

Photosynthesis protein is usually used in photosynthesis bacteria in micro-engineering research. In particular, the protein in photosynthesis reactions in past research exhibit oxidation reduction functions by releasing electrons through light absorption. The target in this research is the creation of a reactor that allows oxidation reduction reactions by rearrangement and reconfiguration. The electrical energy released will be harnessed for enzyme control.

Protein sequence and orientation methods are also studied using recognition bonding functions like abyzin-biotin or antigen reactions in living matter.

Orientation and fixing techniques onto mounts using abyzin-biotin reaction was also developed for chromatophore membrane that includes photosynthesis protein. Orientation and fixing techniques onto solid surfaces at the protein level are also being developed.

2.2 Development of Analytical and Restructuring Techniques for Functional Protein and Lipid Aggregates

Functional protein responding to chemical matter was isolated and extracted from a living organism and its structure and functions were analyzed and evaluated. A chemical signal responding membrane fusion discharge system (exo cytosis system) for microcell reactor application was created by organically restructuring artificial lipid bimolecular membranes. The high sensitivity and amplification features of the microcell reactor shown by the large discharge generated by a small amount of stimulant are industrially promising. Joint research with Kuraray Co., Ltd., artificially reproduced the mechanism of information transmission and amplification in ecso cytosis. Its applications were developed.

An experimental membrane fusion system that can be reproduced with good results was established using membrane fusion protein. Microscopic images of the membrane fusion process were successfully detected and analyzed with the help of a fluorescent microscopic image detection device.

2.3 Basic Properties of Functional Lipid and Protein Aggregates

A new lipid molecule was designed with glycolipid as the model and optimized for mass synthesis. Methods were established to fabricate nano size μm membranes from the synthesized lipid. The helix peptide structure in lipid and the effects of lipids on thermal stability of the solid structure of membrane protein were confirmed through various measurements. Thus, fabrication techniques for molecule membranes with the optimum performance and configuration required in a nano size membrane reaction vessel and at the same time, design guidelines for high-performance protein molecule aggregates, were established.

Intermolecular forces were measured through design and synthesis routes for new lipid molecule groups and analysis and evaluation methods for lipid. The peptide's helix structure in lipid was confirmed and methods were also established to analyze the thermal stability of higher structural orders in water soluble protein.

2.4 STM Research on Microstructure of Functional Protein Aggregates and Function Evaluation Method

The scanning tunnel microscope (STM) that allowed atomic to molecular observation of surfaces of metals and semiconductors had a big impact on surface science and surface material development. STM may be applied to

organic substances, living membranes, and protein aggregates since observations are possible in vacuum, air or in liquid. However, problems like sample setting or scope of vision (view) determination, are anticipated in applications to the abovementioned materials as their conductivities are significantly lower than semiconductors or metals.

This project therefore developed an STM with complementary optical microscopic function and atomic level resolution of 10 μm view angle. Protein, whose structure and liquid crystal state are understood, was then observed. A method to fix organic matter onto a stable mount was developed by fixing the aggregate on the gold (111) vapor deposited plane of mica. Surface treatment methods that include chemical modification methods, are currently being developed for general applications.

2.5 Development of Nano Probe Technology for Structure and Function Analysis of Molecular Aggregates

The atomic force microscope (AFM) is a new type of microscope that allows observation of the microstructure on the surface of a sample by measuring the very weak two-dimensional surface force (of the order of 10^{-10}N) between the sample and the probe attached to the end of a micro cantilever. In principle, this microscope should also be applicable to the observation of samples that are electrically nonconductive (insulators) since there are no restrictions on the sample. Another type of AFM for observing molecular aggregates active in a liquid medium was also specially developed in this project. Thus, the functions and structure of protein and lipid aggregates can be performed at the atomic and molecular level.

An AFM device that can operate under a liquid environment was successfully developed using the optical lever method. This device was confirmed through observation of the mica sample mount in water to have an atomic level resolution.

2.6 R&D on Photoreaction Control by Physico-Chemical Methods

The purpose of this R&D project is to develop general-purpose orientation structure control techniques and restructuring techniques that allow future applications in various types of protein membrane. The main material used will be the photosynthesized bacteria while the main handling technique will use the physical force (field) and boundary chemical force (field). In other words, studies are currently being done on the structuring and fixing of photosynthesized protein aggregates that exhibit electrooptical exchange activity and are deposited in a high-activity state by either the electrical deposition method or the LB membrane method onto a two-dimensional electrode mount made of either metal or semiconductor. A laser trapping device equivalent to a pair of pincers in the form of light and evaluation techniques for regularity in the arrangement of the fixed protein aggregates were also developed. The target now is to create a model reaction system that can control the activity of the protein by light itself.

Photosynthesized protein aggregates using the LB membrane method and restructured in ribosome by the electrical deposition method were successfully fabricated into thin membranes. An optical tweezers (laser trapping) system for photosynthesized protein aggregates is currently under development.

2.7 R&D on Photoreaction Control Systems by Biochemical Methods

This project aims at understanding the mechanism in the transformation of light energy into chemical energy in the initial stage of photosynthesis in plants, and then developing applications based on the results. In this reaction, the focusing chromatographic protein aggregates that exist in the photosynthesized membrane first concentrate the weak sunlight to make the photochemical system II protein aggregates to decompose water to release oxygen, protons, and electrons. However, this type of protein aggregate is very unstable and thermophile cyano bacteria (kelp) was studied as a source of stable protein aggregates. The water decomposition mechanism in photochemical system II protein aggregate by light was analyzed and ways to stabilize the system were studied. In addition, creation of energy production systems, analysis of optically synthesized membranes, design of artificial membranes, and the analysis of concentration and effective conduction mechanisms for light energy in focusing chromoprotein aggregates phycobilin were also studied.

The cloning and primary structure of genes in Mn stabilized protein that contribute to water decomposing reactions were determined. The primary structures of two subunits of focusing chromoprotein and phycocyanin were determined and the properties of the three-dimensional structure are currently being studied. Lipid and adipose tissue that constitute a photosynthesized membrane were analyzed.

2.8 R&D in Molecule Recognition Control Reaction System for Micro Membranes

Directly bonded ion channel neuro receptors are molecule recognizing protein that exist as a receptor and an ion channel inside the molecules of the membrane of a living organism. Ligands in glycine, GABA_A (α -amino butyric acid) and glutamine acid were identified while the mechanism for Cl⁻, Na⁺, and Ca²⁺ ion transmission was clarified for development of basic technical application techniques. Change, design, and extraction of receptor protein, synthesis of various artificial phosphorous adipose tissues, and restructuring and observation techniques by STM were developed.

Bovine brain GABA_A receptor gene was extracted to generate a secretion and expression system outside the cells of bacteria in the large intestine. Various receptor antibodies and mutated Glu receptor that originated from rat brain were fabricated and evaluated. Synthesis of adipose tissue, restructured protein and lipid, sharpness of edge of probe of STM and protein observation method were also studied.

2.9 R&D in Ecto Cytosis Molecule Recognition Control Reaction System

We sought to analyze the various factor processes using membrane models in living organisms and express their performances by developing ways to perform visualized analysis on dynamic membrane changes in model follicle system and cell and on dynamic processes in molecule recognizing discharging phenomenon through analysis of the optical time. Separation techniques for functional protein that respond to various molecule and electrochemical stimulations were also developed together with modification methods that allow optimization and control of the fusion phenomenon. In this manner, membrane fusion and bridging between the membranes became possible. As a final step, the aforementioned restructuring simulative techniques were combined and the creation of an immediate response fixed quantity discharge system for reactive tissues by molecule recognition became possible through testing and evaluation of several reaction control application systems.

Several types of partial peptides equivalent to IgE bonding were synthesized by adjusting soluble Fcε receptors that behave as triggers in ecto cytositis phenomenon. Methods to adjust stable ribosomes with homogeneous particle size and methods to evaluate the stability and membrane fluidity were established.

2.10 R&D on Endo Cytosis Type Molecule Recognition Control Reaction Systems

This project analyzes the overeating mechanism on a macrofuzzy basis as part of applications of functional protein aggregates, and by identifying the necessary constituent tissue groups, develops a method to restructure all or part of the artificial microstructures observed in the mechanism.

The mobility peculiar to animal cells are typified by the macrofuzzy processes in higher animals which are closely related to the nonspecific overeating effect, selective overeating effect to a certain extent and to immunity response. Such macrofuzzy characteristics may be applied to techniques that employ the relatively simple tissue selection property when functional protein aggregates are used.

Several conditions for increasing the quantity of such protein expressed by activating Fcγ receptors were identified and at the same time, monoclonal antigens in calcium bonded protein believed to contribute to the macrofuzzy overcolored effect were fabricated.

2.11 R&D in Functional Composite Lipid Synthesized Enzyme Aggregates

Functional composite lipids like glycolipid exist on the surface layer of cells and are closely related to cell functions like recognition of outside information, membrane functions, modification of membrane protein functions, bonding factors in cells, and receptors in virus or bacteria. This only exists in the body in minute amounts and since reactions in the different membrane enzymes are in several stages, research on their physiological functions and applications are still few. Similar reactions can be more effectively performed by sequencing the necessary enzymes, once they are available, onto the artificial double-layered lipid membrane.

The purpose of this project is to artificially recreate the functional composite lipid synthesized enzyme aggregate and to fabricate a system for synthesizing the complex functional composite lipid. Factor techniques required for extracting, isolating, and refining the necessary membrane enzyme from a living organism were developed for their recreation onto a double-layered lipid membrane.

Success was achieved in making UDP-glucose:ceramide glucose metastasis enzyme in the first biosynthesis reaction stage in glycolipid soluble. Methods to reactive and partially refine the enzyme by recreation was also successful.

2.12 R&D in Genetic Engineering Methods for Composite Oxidation-Reduction Systems

The purpose of this project is to create extremely effective, stable, and functionally positioned composite oxidation-reduction systems like oxidoreductase and electron transport enzyme systems. It also aims at the development of ways to control the localization and orientation of the membrane enzymes. Establishment of this system will enable advanced application of enzyme functions that exist locally in membranes of living organisms thereby expanding the scope of applications to production of various useful tissues.

In the first and second phase of this project, the major factors and indicator protein that contribute to the integration of choline bacteria onto the membrane of the membrane protein, were cloned. In Phases Two and Three, the parameters affecting quantity integrated onto the membrane protein was studied and those factors that enable effective control were identified. Studies were also done on the factors affecting integration onto the membrane of the membrane protein and the fluctuation in the integrated quantity which were investigated through modification and stabilization of factors that adjust the membrane content in the membrane protein. Recreation methods were also studied.

DNAase gene that acts as an indicator for analyzing the change in quantity of choline bacteria integrated in the membrane protein was cloned. Basic conditions for cloning SEC protein genes that affect integration were also established.

3. Conclusion

Establishment of handling and reproduction techniques for functional protein aggregates typified by membranes in living organisms and cell organs had not only allowed application of useful functions in single enzyme molecule of the various advanced functions in a living organism (energy transformation, tissue reproduction, tissue transformation, tissue transport, selective transmission, information recognition, information transmission, tissue recognition, motion, etc.) that were impossible in past applications, but has also made inroads into the artificial strengthening, amplification and application of those techniques thereby promising significant results in the field of bioindustry and accelerated application to the biotechnological mining industry.

R&D in Compound Sugar Production Application Technology

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[Article by Professor Ogawa, Department of Agriculture, Tokyo University]

[Text] 1. Introduction

This 10-year project which began in 1991 as part of the Jisedai Project has six private corporations and three national research institutes as participants.

Compound sugar is a basic constituent in the living organism and has important functions like matter recognition—functions that cannot be duplicated by nucleic acid, protein or fat. Nucleic acid, protein and fats have already been the subject of much study and numerous products are available in the market. Studies on compound sugar, however, are very limited because of its complicated production control mechanism, complicated structure, and diverse glycol chain. Advances in recent research and development techniques and knowledge accumulated on the glycol chain has helped studies to proceed into the realm of glycol structure, functions, and synthesis methods.

The purpose of this project is to establish the fundamental techniques related to mass production of compound sugar for industrial purposes.

2. Synthesis, Application, and Modeling Techniques for Compound Sugar by Chemical Methods

2.1 Basic Studies on Material Functions Through Introduction of Glycol Chain

The effects of introducing a glycol chain on the functions of a material were studied. Physiologically active compound sugar was extracted from a living organism and the relationship between its structure and functions were investigated. That part of the structure that contributes the most to physiological activity is adjusted by synthesis or partial refinement and then bonded on the material surface, in particular, the surface of synthesized high-polymer materials in such a manner that the physiological activity does not drop specifically. A material whose functions are expressed in the same manner as in a living organism can thus be fabricated.

Next, the cell culture reproductivity and its functionality, biosegregationality, and biocompatibility are investigated for materials whose functional compound sugar are bonded. Cell culture materials for hybrid artificial organs, chromatography beads with high specificity, materials for bioreactor and biocompatibility materials are generated and their functions studied.

The final purpose of this project is the development of fundamental techniques for identification applications of materials modified by functional sugar.

2.2 Synthesis, Application, and Modeling Techniques for Compound Sugar by Chemical Synthesis Methods

In this study, the glycoprotein sugar chains are assumed to be several pieces of oligosaccharide fragments which are synthesized by the enzyme synthesis method. These oligosaccharide blocks are then chemically synthesized into sugar chains. Sialic or fucosic base side chains can be bonded whenever necessary with the help of metastatic enzyme. Glycoprotein can be created when this sugar chain is bonded to protein.

Natural sugar chains will be created when sequences of oligosaccharide blocks that exist in nature are employed but when the sequences do not exist in nature, nonnatural sugar chains will be created. Once the sequence of the sugar chain that exhibits a certain function can be designed, synthesis of the chain can be extremely simple because procedures follow the design diagram. This method is thus best for remodeling.

The following are some of the issues hampering progress in this project.

- (1) Search for the microorganism that produces the glyco hydrolase required for oligosaccharide synthesis.
- (2) Oligosaccharide synthesis by enzyme synthesis method.
- (3) Oligosaccharide block bonding by chemical synthesis method.
- (4) Sialic and fucosic base side chain bonding.
- (5) Sugar chain bonding to protein.
- (6) Isolation and refinement of synthesized sugar chains and glycoprotein.
- (7) Molecular design for highly-advanced compound sugar (in-charge by another group).

These issues were investigated for N-glycoside and O-glycoside sugar side chains. Remodeling techniques were thus completed by synthesizing the designed sugar chains with an assumed set of functions.

2.3 Design of Compound Sugar Molecules

An understanding of the effect mechanism at the molecular level is essential for realizing the final target of this project—compound sugar remodeling. Therefore, molecular design and structure determination methods are also developed in this project.

2.3.1 Molecular design

- (1) Molecular graphics: basic connection between researchers and computers.
- (2) Solid structure database: database on solid structure of known compound sugar related molecules and development methods to construct the whole solid structure from basic partial structures.
- (3) Molecular mechanics computation: important for handling complex molecules like compound sugar. Existing software is defective and should be improved.
- (4) Quantum mechanics computations: employed for setting parameters and analyzing enzyme reactions because the semi-experienced method is unsuitable for handling sugar molecules and the inexperienced is time consuming.

2.3.2 Molecular structure analysis

- (1) Sugar chain sequence: important for developing molecular design techniques from experimental samples. Develop analytical techniques as a tool for establishing communication ties with other research groups.
- (2) Solid structure: there is insufficient experimental data on the solid molecular structure of compound sugar. Nuclear magnetic resonator (NMR) analytical techniques will be developed and ways to link this to molecular design will be studied.

3. Biological Synthesis, Application and Remodeling Techniques for Compound Sugar

3.1 Basic Studies on Compound Sugar Synthesis Using Animal Cells

Compound sugar like glycoprotein is extremely important as an intermediate substance in biofunction control substances and medical drugs. Its structure is extremely complicated and as a result, production of the desired substance cannot be achieved with current technologies. As a result, the biggest hurdle is cell engineering in compound sugar structure control.

In this project, cultured animal cells, particularly human cells, are used to establish basic technologies for producing useful and new glycoproteins.

First, establishment of biological synthesis and application techniques for compound sugar is achieved by nurturing useful long-living cell stocks from animal cells, particularly human cells and then transforming them into stocks that can be cultured in serum-free medium or completely protein-free medium. The cells are then evaluated for effective introduction in human genes so that new host cells for compound sugar production can be generated. The human cells conditioned medium liquid is also studied in the search for new compound sugars.

Next, human cell variant stocks are isolated for biosynthesis of compound sugars. These stocks are employed in the development of compound sugar mass production systems with the help of human cell stocks. Compound sugar is then isolated and refined and the resulting amino acid sequence and sugar chain structure are analyzed. The biological functions are assessed through reproductive and modifying functions expressed in cultured animal cells.

Finally, functions are assessed for synthesis of high-function compound sugars, by the existence of sugar chains or modifications in its sequence when the sugar chain is biochemically modified.

Fundamental technologies are thus established for production of high-function compound sugar using animal cells.

3.2 Compound Sugar Synthesis, Application, and Remodeling Techniques Using Animal Cells

The purpose is to establish uniform and highly effective production methods for industrially useful glycoprotein of a certain purpose by controlling enzyme groups at the genetic level that contribute to the various culture conditions or sugar chain biosynthesis within cells, with the help of plankton cells. In the beginning, evaluation and structure synthesis methods were established for sugar chains using immunoglobulin as the model protein. Then, various culture conditions were studied for developing a more uniform and effective production method for the desired useful protein. Other plankton cells were also investigated for use as host cells while the sugar chain diversity depending on the host cell was also studied. The added sugar chain diversity control was also investigated through control of the quantity of enzymes expressed, at the existing compound or genetic level or in other words, enzyme group activity related to sugar chain biosynthesis within a cell.

Next, uniform and highly effective production methods were developed for industrially useful glycoprotein through the introduction of new sugar chains into protein that does not originally have a sugar chain or protein that has a sugar chain in the part that does not originally have a sugar chain, as the model for protein production using plankton cells.

3.3 Basic Studies on Compound Sugar Synthesis Using Yeast

First, a yeast variant which can synthesize only a core type sugar chain was isolated because of the defect in additional reaction in the mannose outer

chain. At the same time, the chemical structure of the sugar chain was also analyzed, the gene for recovering the variant of the above yeast variant stock was isolated, and the genetic structure and functions coded in the protein are analyzed. As a result, supply of yeast variant stock for producing intermediate substances (glycoprotein with core sugar chains) for transformation onto human sugar chains or useful metastatic enzyme for mannose metastasis is now possible.

Next, the yeast variant stock (budding or mitotic yeast) is selected to produce specified proteins (for example, TPA or IL6 derived from humans) found in core sugar chains in the nonreduction terminals of mannose or galactose. At the same time, physiological functions in the produced glycoprotein were compared with those in humans. Galactose metastatic genes derived from mitotic yeast was isolated and introduced to budding yeast. Its expression was studied to create a means of supplying intermediate substances (specific glycoprotein in core sugar chain of nonreductive end of galactose) for producing useful glycoprotein observed in human sugar chain.

Finally, the above glycoprotein was introduced in sialic acid metastases genes derived from humans for studying addition of sialic acid to the sugar chain. When the human-derived glycol metastases gene does not express as targeted within the yeast, then the gene is expressed onto a large intestine bacteria and then adjusted for large quantities of glycometastase. This is then reacted extracellularly with the above-mentioned intermediate substance for testing transformation onto human sugar chains.

Useful glycoprotein having new human sugar chain was therefore synthesized using yeast by any of the aforementioned methods.

3.4 Synthesis, Application, and Remodeling Techniques for Compound Sugar Using Microorganisms

The final target is the establishment of basic industrial production techniques for glycoprotein having human sugar chain with the help of microorganisms like yeast.

First, the factor: host side factor (glycol metastases, glycosidase, glycol nucleotide biosynthesized enzyme, etc.) that determines the final structure of the compound sugar and the glycoprotein side (primary structure of peptide, DNA sequence, etc.) were identified for development of methods that allow these factors to be skillfully employed as tools. Techniques were then developed to express these factors as functions of microorganisms like yeast. Parallel to that, methods to modify, in vitro, the sugar chain structure in the compound sugar produced with human compatible functional sugar chains were also investigated with the help of sugar chain biosynthesized enzyme. Progress was also achieved in the development of function assessment methods for compound sugar. The National Chemical Lab for Industry group involved in this project succeeded in generating microorganisms like yeast suitable for introducing to sugar chain biosynthesized metastases gene and its expression by host. Basic research on key reactions in sugar chain biosynthesis will be investigated in the future. Results obtained will be incorporated in the later

phases of this project for developing production methods for human type sugar chains with the help of microorganisms like yeast. Studies related to the structure and functions of sugar chains will also be made and will be extended to remodeling techniques or design and production of ultrahigh function compound sugar.

3.5 Analysis of Structure of Compound Sugar

It is very important for the primary structure of the sugar chain in compound sugar produced using animal cells or yeast to be speedily analyzed and the results fed back into the production process. A rapid analytical method for primary structure of sugar chains was thus developed using specific molecular recognition mechanisms in biomolecules. In particular, this project aims at supporting the effective development of biological production and aggregate techniques for glycoprotein. Speedy methods to check if a sugar chain is correctly introduced into the right place during remodeling of the compound sugar were also studied. Molecular design for remodeling and its accuracy are also part of studies in this project.

Lectin and monoclonal antibodies are known to be sugar chain specific recognition substances and some are highly sensitive detectors. This project also used lectin and monoclonal antibodies to develop methods to analyze the sugar chain structure in compound sugar.

The specificity in lectin and monoclonal antibodies are studied and the sugar chain recognizing substances believed useful for structure analysis are identified and the amount required for analysis is then extracted. Next, methods to free the end sugar chain under neutralizing conditions were developed as a means of successive analysis for the higher order and very complex sugar chain structure. Methods were also developed to analyze the remaining sugar chain structure after release of the end sugar chain. Analytical techniques and its automation were investigated using effective isolation and refinement methods of biosensor methods in attempts to develop accurate, speedy, and continuous analytical methods for the complicated sugar chains.

4. Conclusion

Various molecular level handling techniques for compound sugar found in various functional protein aggregates in vivo were completed in this project.

(1) Protein function improvement: By bonding sugar chains to enzymes, thermal stability and durability of enzymes can be improved thereby significantly expanding the range of applications for enzymes in chemical engineering fields like bioreactors. As a result, productivity of useful substances like fine chemicals is greatly improved.

(2) Activation of recognition capability: By activating the specific recognition property in sugar chain, separated and refined materials like fine chemicals that were conventionally difficult to refine effectively, new biomaterials and biocompatible materials that take advantage of affinity with living matter are some of the successes in this project.

(3) Use of functional sugar chains: Realization of synthesis and supply of large quantities of sugar chains has created new applications for highly advanced and selective biosensors and useful substances like fine chemicals.

Results of R&D on New Functional Devices; Motive Behind Development of Basic Technologies

926C0071T Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 147-154

[Article by Professor Tsurujima, Faculty of Engineering, Kyushu University]

[Text] 1. Introduction

R&D in ultra-grid devices, three-dimensional circuit devices, and environment-resistant reinforced devices were developed as part of the Jisedai Project that was launched in 1981 with the hope of reaping the fruits in the form of foundation industrial technologies in the 1990s. The project is now complete. The project on environment-resistant reinforced devices lasted five years while superlattice devices and three-dimensional circuit devices lasted 10 years each.

This paper will describe the results of these projects and the reasons for the projects.

2. R&D Target and Implementation Program

2.1 Environment-Resistant Reinforced Device

General semiconductor devices and integrated circuits are usually used in a comfortable environment like the living room of a house. They are not necessarily reliable when used under adverse conditions like outer space, around atomic reactors, in plant instruments in very hot surroundings, around mobile parts in aircraft or automobiles, or even conditions that are very hot or subject to mechanical vibrations or impact.

The purpose of this project is to improve the radiation resistance of large-scale integration (LSI) equivalent Si integrated circuits assuming applications in outer space. Another target is the fortification of basic technologies for realizing compound ICs with improved radiation resistance and thermal resistance and key devices, assuming their application in atomic energy or high-temperature environment.

Target achievements for each development are listed in Table 1. In the beginning, development was to last a total of eight years with Phase One taking three years, Phase Two taking two years, and Phase Three lasting three years. However, development targets with the exception of integration scale were nearly completed at the end of Phase Two and as a result, the project was announced complete in FY 1985. Research after that concentrated on real applications and was channeled to other projects in addition to the Jisedai Project. National research institutes were in charge of establishing techniques for assessing radiative effects and the pursuit of SiC as a potential heat-resistant device.

Table 1. R&D Targets for Environment-Resistant Reinforced Devices

Type	Target performance			
	Integration (device/ chip)	RR (rad)	HR (°C)	VR/IR (G)
1. Si IC				
(1) MOS IC CMOS (bulk/SOS)	$>3 \times 10^4$	$\sim 10^5$	>125	
(2) Bipolar IC (IIL)	$>8 \times 10^3$	$\sim 10^5$	>125	
2. Compound semicon- ductor IC				$>40/3000$
(1) RR device (GaAs)	>30	$\sim 10^8$	>200	
(2) HH device (SiC)	>30	$\sim 10^8$	>300	

2.2 Superlattice Device

Progress information processing technologies have greatly improved and consequently demands on the semiconductor technology that supports this has also increased significantly. Advancement of semiconductor device technology will depend largely on large-scale integration of Si ICs and the accompanying decrease in device size.

Unending efforts have been continuously made to rid ourselves of our existing device concepts and to pioneer new technologies for semiconductor devices. Not only normal semiconductor materials that have uniform configuration and structure, but also high performance and customized devices, can be fabricated through crystal constituent or impurity distribution control through band engineering. This has presented interesting issues in the highly attractive long-term development and semiconductor device technologies. The use of various compound semiconductors, heterojunction structures and quantum well structures or incorporation of functions in devices through activation of the tunnel effect or low dimension electron conduction hold great promise.

Technical development of applications related to fabrication of superlattice structures was believed to contribute to the base technologies in Jisedai and was thus implemented.

National research institutes pursued development of base techniques and new device concepts while private corporations were in charge of the development and verification of superlattice functional devices and superlattice structure devices using the electron properties peculiar to superlattice structures.

2.3 Three-Dimensional Circuit Devices

Expansion of the scale or functions of integrated circuits was the focus in the LSI age in the early 1970s, and over the past 15 years, improvements of 1,000 times over were achieved, and are still being made. The biggest factor behind this improvement was the reduction in size of the key factor devices. However, size reduction has a limit because of the finite dimension of the devices and this limit also represents the integration scale limit which is also related to the limit for performance improvement of the integrated system.

Integration limit can be avoided if the space for housing the factor devices can be expanded from two- to three-dimensional space or in other words, performance improvement or diversification of the device can isolate the speed factors. This is the concept behind three-dimensional integration.

This project has raised numerous opinions and discussions on the necessity and meaning of three-dimensional structures for integrated systems. At the same time, fabrication processes for multilayered silicon on insulator (SOI) structures by the fusion recrystallization method or thin film layering method using laser or electron beams, reduced use of or increased degree of freedoms for wiring leads due to three-dimensional layout, accelerated speeds for factor devices due to SOI structure or circuit operations, circuit configuration selection or performance verification suitable for parallel and simultaneous information processing and other possibilities are studied from all aspects. National research institutes have forecast that the realization of three-dimensional configuration will come after the design rule for factor devices have achieved the deep submicron regions. They have thus concentrated on proposals for factor devices and basic guidelines for developing process techniques essential for its realization.

3. Results

3.1 Environment-Resistant Reinforced Devices

The biggest radiative effects on normal metal-oxide semiconductor (MOS) and Si integrated circuits (ICs) is the accumulation of position electrical charges inside the insulative membrane like SiO_2 and the generation of a boundary potential at the insulator membrane/Si crystal boundary. This leads to increased threshold voltage fluctuation and leak current in transistors. The purpose of this project is the reduction of threshold voltage fluctuation due to thinning of membranes as a result of temperature drop and membrane

oxidation throughout the whole process. It also aims at the optimization of the temperature (900°C) for fabrication of the oxidized membrane. This project has succeeded in suppressing leak current increase to a minimum by partially altering the structure of the transistor. The fluctuation margin for the threshold voltage in the transistor was expanded and circuit design was improvised to reduce leak current. A 64-bit complementary metal-oxide semiconductor (CMOS) with 1,000 devices was thus designed, verified and was confirmed to be able to endure continual γ radiation of more than 3×10^5 rad.

Bipolar integrated circuits represented irradiation effects in the form of rate of electric current amplification and reduction in operation speed. This project employs a double film layer structure—thin oxidized film fabricated at high temperature on a relatively thick surface insulator layer and a thick oxidized film fabricated at low temperature—and has succeeded, by assuming the base of oxidized film to be a high concentration layer, in creating transistors that are about 50 times more radiation resistant. The trial-produced ring signal generator with 686 tensile strengths devices was verified to have γ -ray irradiation resistance of more than 2×10^5 rad.

NF properties in GaAs analog ICs are affected by irradiation and normally deteriorate at about 10^7 rad. This was improved. In this project, by improving the structures of gate electrodes or channels and understanding the effective process conditions for improving radiation resistance. The X-band amplifying GaAs analog IC thus trial-produced was confirmed to operate up to 10^8 rad. Similarly produced medium scale integrated circuit (MSI) level digital IC was found to have resistance up to more than 10^8 rad.

Much knowledge was accumulated on standardization of radiation conditions and radiation evaluation as well as evaluation conditions for composite environment. In SiC heat-resistant device fabrication, solid crystal SiC crystal film was grown and the process for fabricating MOS transistor as well as a test device was successfully fabricated.

3.2 Superlattice Devices

The establishment of methods to control crystal growth at accuracies of single atomic planes is vital for widespread superlattice applications. The phase control epitaxial method was developed as a common base technique to control crystal growth by feeding the intensity vibration signal in the reflected high-speed electron diffracted beam while growing the molecular beam epitaxy (MBE)-crystal back into the molecular beam supply system. It was confirmed to be highly effective for accurate atomic level growth control in superlattice structures like SiGe or various compound semiconductors. This result was widely applied in the later stages of this project as well as in other projects. Figure 1 shows the configuration of the crystal growth device that uses the phase control epitaxial method.

Development of superlattice functional devices was based on the resonant hot electron transistor (RHET) proposal based on a new operating concept of introducing a resonant tunnel obstacle structure in a part of the emitter in the hot electron transistor. Its effectiveness was confirmed. Generation of a

negative derivative conductance in the device as a result of the hot electron source in the form of resonant tunnel wall obstacle shows great promise for future increase in speed, performance, and integration of very-large-scale integrated circuits (VLSI), demand for which is expected to increase. Figure 2 shows the cross section and band structure for RHET. One of the strong points in integrated circuits using RHET is the possible realization of circuit performances with fewer devices. For example, an adder using RHET will only have about one-fourth of the total number of devices when compared with conventional bipolar transistors.

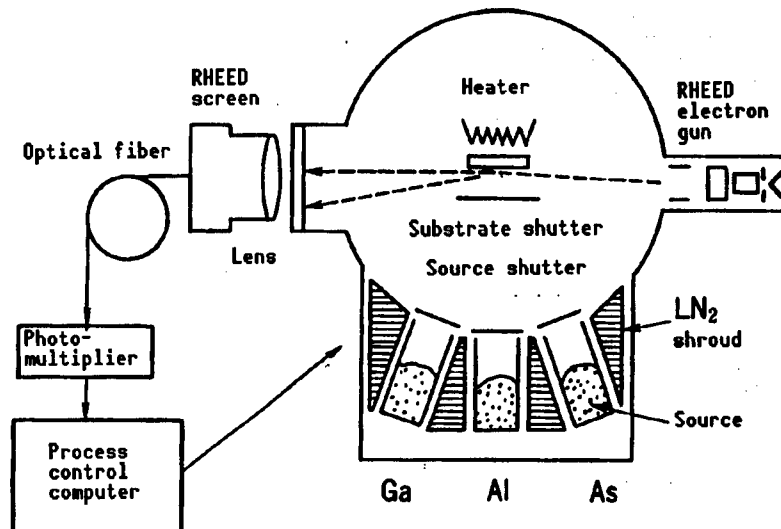


Figure 1. Concept Diagram for Phase Control Epitaxial Crystal Growth Device

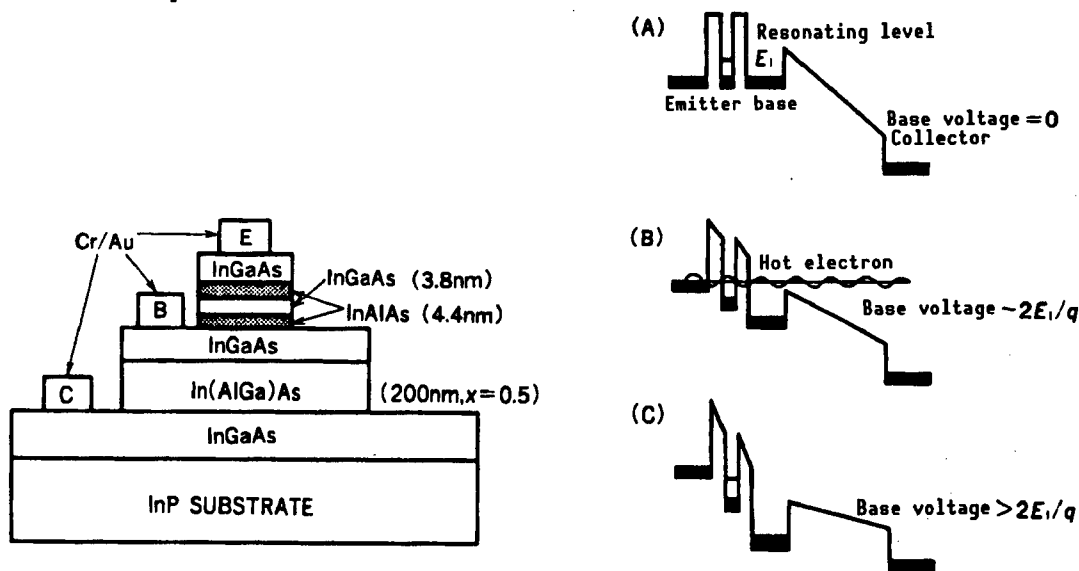


Figure 2. RHET Cross Section and Operation Principle

It was also confirmed that the metallo-organic chemical vapor deposition (MOCVD) method can accurately control crystal growth at the atomic level. This result was successfully applied to the test fabrication of room temperature operated GaSb/InAs HET with current amplification of 8. A modified doped field effect transistor (FET) using properties peculiar to short frequency InAs/GaAs superlattices was also trial produced. It was confirmed to have mutual conductance of 475 mS/mm and cut-off frequency of 28.5 GHz.

Development of superlattice devices was achieved through methods for burying Si/CoSi₂/Si double hetero single crystal structures that have smooth and steep boundaries and through silicide self-diagnostic growth methods. A completely buried type Si-PBT test sample with submicron dimensions was successfully fabricated where $g_m = 50 \text{ mS/mm}$, current density = $2 \times 10^4 \text{ A/cm}^2$, and $f_T = 6 \text{ GHz}$.

3.3 Three-Dimensional Circuit Devices

The basic technology for this device is the fabrication of multilayered SOI structures. Results achieved in this project are diverse in the form of optimization of irradiation conditions and beam shape in fusion recrystallization method using laser or electron beam, clarification of rotation mechanism along the crystal axis during recrystallization process, and determination of its azimuthal control, process conditions for low temperature solid phase crystal growth in the horizontal direction and clarification of conditions for high-quality GaAs on Si heteroepitaxial film growth and finally in the form of development of the CUBIC method where thin films of polished double-layer structures made of monolithically SOI layer attached to the bulk crystal layer are laminated together.

Significant process was also achieved in device fabrication processes like the three-dimensional layering of heat treatment leads made of metals with high-melting point, fabrication of electrodes with low ohmic resistance, fabrication of throughholes with high aspect ratio and their burying techniques and finally the establishment of flattening techniques for interlaminary insulating layers.

Three-dimensional circuit structures were proved effective in chip performances with the help of a four-lamina SOI structure in the form of a three-dimensional real-time image processor in a 64×64 image detector for detecting object shapes, an image processor with built-in sensor for detecting moving objects, character recognizing processor that can compare the input information with its stored character memory and make decisions. All these applications confirmed the significant leap in simultaneous and parallel pattern information processing speed by three-dimensional integrated circuits. the integration scale is currently 100-300 K devices/chip. Figure 3 shows the configuration of the object shape determination processor and the operation concept using the light-interception method.

The XMOS transistor with its cross section shown in Figure 4 was proposed as a three-dimensional factor device that can operate at deep submicron regions. This device was confirmed to have superior properties through a one-fourth μm test sample and performance verification tests. It was also effective in reducing short-channel effects due to reduction in size and increase in detail. Reduction limit for MOS device was extended to below $0.1 \mu\text{m}$. A synchrotron with a positioning accuracy on the order of $0.01 \mu\text{m}$ was also developed as part of the process technology developments that are essential in fabrication of such minute devices. Several new focusing ion beam processes were also developed.

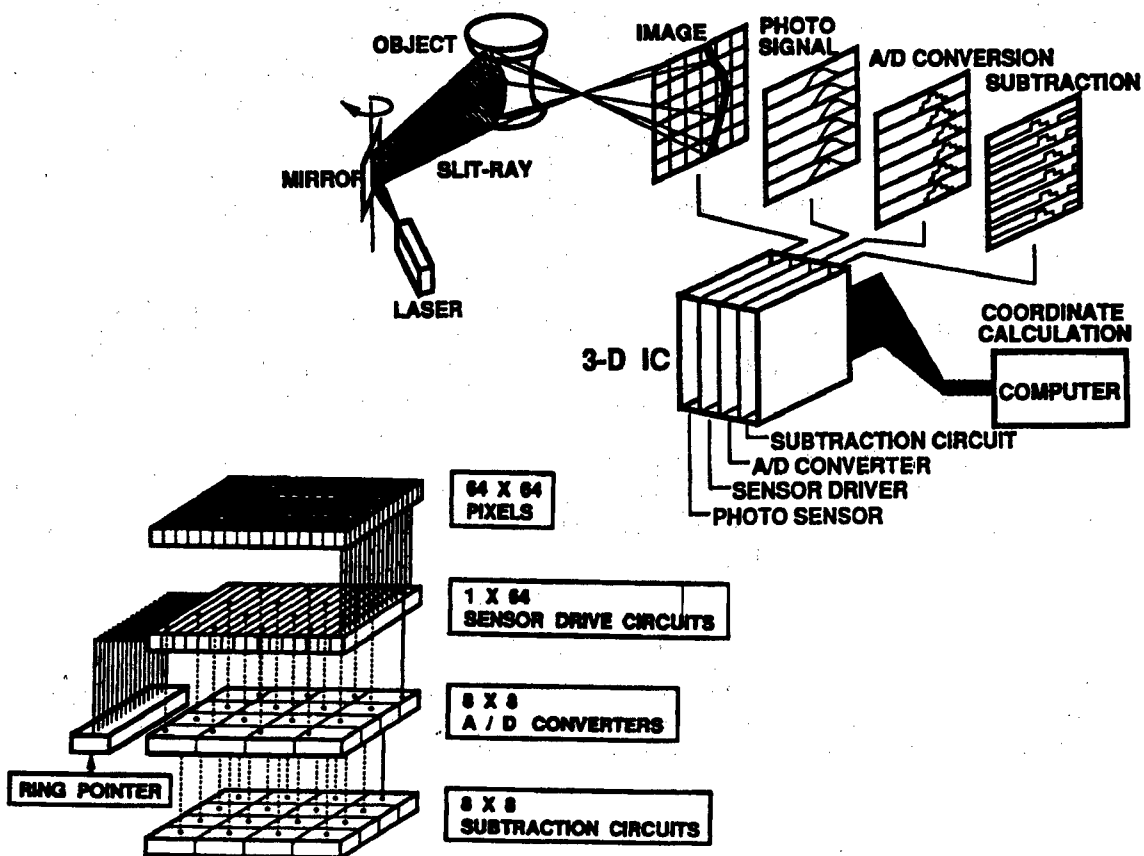


Figure 3. Function Block Configuration for 4-Layer 64x64 Pixel Image Processor and Its Application to Three-Dimensional Shape Measurement by Light Interception Method

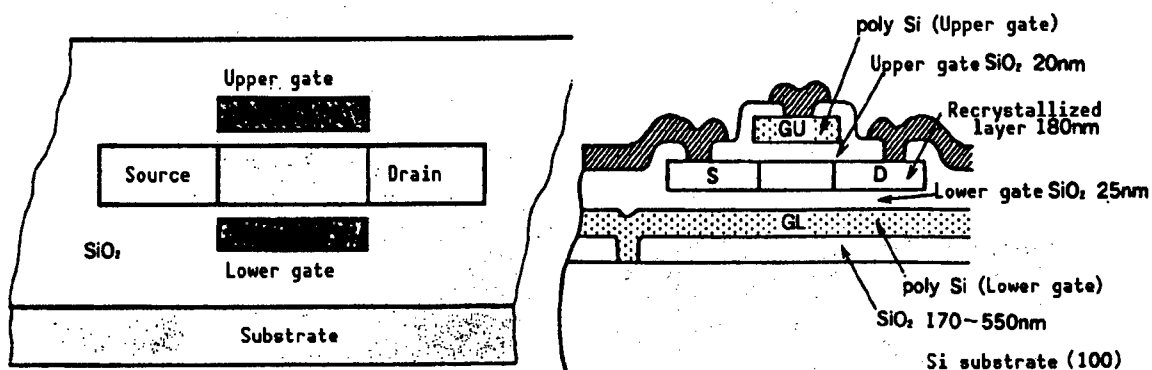


Figure 4. Cross Section of XMOS Transistor

4. Conclusion

The Jisedai Project motto of "from seedling to young tree" at the time of its implementation was like a breath of fresh air for expanding the scope of basic research. My interpretation of these words are "nurture potential techniques to a level where their effectiveness can be verified." Verified results are hopefully positive but this is not necessarily forecast. Negative results may also be obtained.

Most criticism of Japan's technical developments from the United States and Europe is based on the fact that Japan has not invested her share in establishing basic techniques. The Jisedai Project, on the other hand, is Japan's contribution to development of basic technologies.

This project has produced new insights and methods in new technical fields and will contribute significantly to basic technologies. Most results are breakthroughs in the field of microelectronics and will further improve existing semiconductor device technologies.

R&D in Biodevices

926C0071U Tokyo SEKAI NI HABATAKU JISEDAL PUROJEKUTO in Japanese 19 Feb 92
pp 155-159

[Article by Masuo Aizawa, professor, Life Science Engineering Department,
Tokyo Institute of Technology]

[Text] 1. Introduction

Biodevices are called dream electronic devices because they are ephemeral and aim at an ideal condition. They are nowhere near realization. Nevertheless, biodevices will become the ideal electronic device.

Biodevices attracted attention in the early 1980s when the words biochip and biocomputer became popular. The Jisedai Project titled "Biodevices" then commenced when the overheated biofever subsided in 1986. Unlike other themes in the Jisedai Project, the "Biodevices" project was launched without clear definition of the targeted biodevices and placed Japan ahead of other nations. The launching of this national biodevices research greatly impacted the United States and Europe because of Japan's lead in beginning basic research on a theme that has an unknown future.

The "Biodevices" project has completed Phase One which lasted five years and is now entering Phase Two. Government support and funding in such grassroots level research is very important. Numerous results have been reported and developments in Phase Two will be closely followed by all nations.

2. "Biodevices" Project

Phase One of this project had the following ultimatum:

- (1) Development of molecular configuration techniques.
- (2) Clarification of bio-information processing mechanism and establishment of a model.

Phase Two emphasized the following in an attempt to develop "neurodevices."

- (1) Conduct research on biodevices technology.

(2) Clarification of bio-architecture and the establishment of an engineering model.

There are two main targets in this project as shown in the project framework. The first, realization of biodevices in the form of molecular devices that take advantage of the properties peculiar to molecules, and the second, determination of bio-architecture from an understanding of information processing mechanism in the brain.

Numerous molecular devices have been proposed as biodevices. Some are not peculiar to molecules in the true sense but they are unique from the point of molecular introduction into electronic devices. Development of molecular configuration techniques are extremely important in the realization of biodevices in the form of molecular devices. A major result of this project is the progress achieved in molecular configuration techniques based on Langmuir-Blodgett (LB) film technology.

A very convincing theory is essential for determining bio-architecture by describing the information processing mechanism in the brain. The development of nondestructive and nonprobing methods to measure signal transmission in fragments of brain tissues is one remarkable result of this project.

3. Molecular Configuration Technology

Tissues in vivo are collections of various molecules. Studies were made on various methods to fabricate molecular structures assumed to be the basic item in vivo.

The Electrotechnical Laboratory researched molecular configuration techniques based on the LB method and liquid phase epitaxial method. Superstructures can thus be fabricated by laminating various lamellar configurational layers by these methods.

Kagaku Gijutsu Kenkyujo focused on the flexibility of molecular configurations in vivo and succeeded in realizing molecular structures that allow easy structure transformation and/or phase transition. Such molecular structures were possible because of the existence of regular spaces of about 5-10 Å.

Mitsubishi Kasei fabricated porphyrin domain structures in single molecule membranes made of mixed lipid acid (arachic acid) and porphyrin.

Hitachi made monoclonal antibodies in tocorodopsin to fabricate protein tissues.

4. Creation of Biodevices

Significant progress was made in fabricating functional molecular tissues and hence the realization of biodevices by employing molecular configuration techniques.

Kagaku Gijutsu Kenkyujo synthesized a stimulant receptor in each molecule, a stimulant transmitter and functional molecules. These molecular structures were photosensitive with changes in their electrical conductance. This molecular structure was proposed for use as a lightswitch device. It also attracted attention as a molecule that responded to input information by processing that information within the molecule itself. Chemical modification of the stimulating receptor made it receptive to a wide range of wavelengths thereby making the design of multi-input devices possible. Chemical modification of stimulant transmitters will enable plastic contribution. There are high hopes in the realization of "neurodevices" targeted in Phase Two.

Mitsubishi Denki (Electric) applied molecular electronic functions in bio-electronic transmission systems for realizing basic functions in biodevices. A rectifying device was thus realized by using flavin porphyrin molecular membrane structure. Metal injection molding (MIM) device was fabricated with similar molecular membrane structure. Highly effective photoelectric transformation was thus achieved. In Phase Two, the electron transition property in heterojunction was controlled by an external electric field for realizing electric field switching functions. Studies are currently under way on the fabrication of multiple input devices by increasing the number of input electrodes for control signals. An image sensor model using flavin porphyrin LB membrane heterojunction (MIM) device is currently being trial produced.

Mitsubishi Electric fabricated bacteriorhodopsin molecular oriented LB membrane. About 20 percent of violet membranes swarmed onto vapor-liquid boundary by normal methods have reverse orientation and application of an electric field during swarming creates a membrane with almost perfect molecular orientation. Electrolytically polymerized membranes can fabricate electrochemically plastic devices. Phase Two aims at the development of nonlinear vibrators which closely resemble bio-information processing devices.

Sharp developed sense information processing devices that recognize smell information by optical pattern recognition. Phase Two emphasizes the development of neurodevices for the pattern information processing part of the device. The plasticity of neural functions using nonlinear photochromism in chromatic associations was also studied. Irradiation of visible light onto molecular associations of spyropyrans splits the association into monomer spyropyrans by the photochromic reaction. Fragmentation of the association reduces light absorption. Association has a threshold value since it does not respond to weak light. As a result, plasticity is realized by recording the multiplication of two light signals below the threshold value using chromatic association. Sharp's biggest challenge is the creation of photo neural devices that optically combine plastic devices and threshold value devices.

Mitsubishi Kasei uses molecular structures to create visual information processing devices that have pattern recognition and memory association properties. The photoelectric transformation layer in the visual information processing device is self-configured domain porphyrin with an array structure. An electrical signal is independently released from each domain when pattern signal is irradiated onto the device. This signal is transported to the

network of pseudo neural devices for high-level information processing like recognition and memory association. The pseudo neural device is made from three layers: input layer, plastic layer, and output layer. The plastic layer "learns" and then "memorizes" while the output layer manages the threshold I/O transformation. A prototype device made of a combination of memory type photo-conducting electrical layer and liquid crystal layer is already available.

Matsushita Giken fabricated thin membranes by vacuum vapor deposition of lead phthalocyanine cones. This thin membrane device has a new switching property. By assuming this property as a temporal synapse plasticity, a simple perceptron circuit was trial produced using this thin membrane device.

5. Challenges in Bio-Architecture

Clarification of learning and memory processes in brains of mammals will be a giant leap in the creation of ultraparallel and ultradiverse learning information processing systems. Denshi Gijutsu Sogo Kenkyujo is challenging the neural circuits in the nervous system of seahorses. A strong weapon is the noninjection, multiple point (16,000 points) simultaneous real-time optical measurement method developed for determining brain activity. Application of this method to seahorse brain helped visualized activity of neural circuit related to long-term amplification phenomenon through spatial and time pattern changes. It is hoped that this study will contribute to a better understanding of the basic physiological processes during learning.

NEC theoretically analyzed the biodata on the brain and attempts to determine the theory behind view computation and synapse plasticity. Phase Two focused on spatial frequency and properties of visual systems like feedback junctions and was successful in establishing a visual model.

Fujitsu concentrated on recessive neurons in the cerebellum that plays a major role in learning and application during motion and has proposed a multilayer neural circuit model.

6. Conclusion

Phase One of the "Biodevices" project has been completed and strong fundamental as well as numerous "seed" technologies were established. Great hopes are placed on further developments in Phase Two.

R&D in Quantum Functional Devices

926C0071V Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 161-166

[Article by Sakamoto, laboratory director, Micro Structure Electronics,
Electronic Devices Department, the Electrotechnical Laboratory]

[Text] 1. Introduction

The amount of information to be processed in the 21st century of the "advanced information age" is expected to increase sharply. As a result, the demand for the development of new ultrahigh-speed, high-capacity, and new-performance electronic devices will also increase. Progress in information processing to date was supported by increased integration with smaller devices. For example, dimensions of the dynamic random access memory (DRAM) silicon device was reduced in accordance with the proportional shrinkage law. As shown in Figure 1, the scale of integration was improved at a speed of about four times in three years. Today, 4M-bit DRAM (metal-oxide semiconductor (MOS) transistors with gate lengths of less than 1 μm) are commercially available and if the current speed of progress is maintained, integration of at least 1G-bit (gate length is 0.1-0.2 μm range) is possible using existing device structures by the beginning of the 21st century.

Performance improvement by the proportional reduction principle and manufacturing techniques which were effective at dimensions above 0.1 μm will face difficulties when characteristic dimensions reach below 0.1 μm .

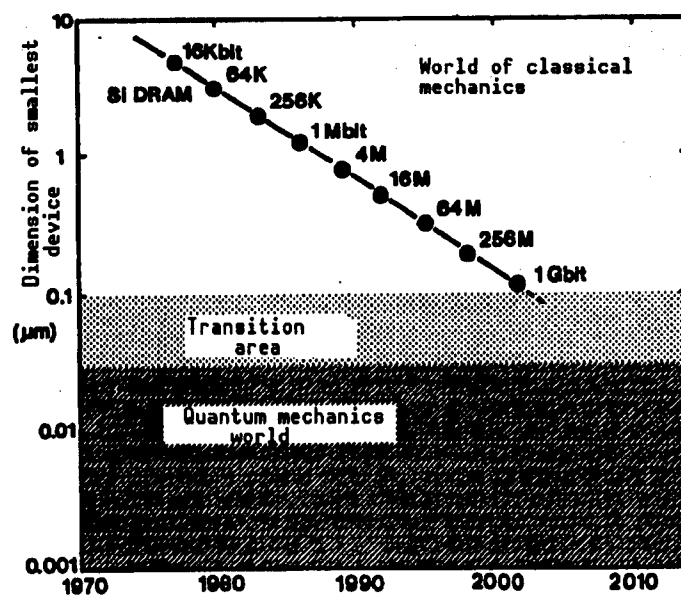


Figure 1. Shrinkage in Device Dimensions
With Respect to Dynamic Memory

Thus, quantasized functional device project was positioned as a breakthrough technology. The purpose of this project is to develop basic technologies for realizing new functional devices using the working principle for various quantum phenomena occurring inside semiconductor microstructures with characteristic dimensions of less than $0.1 \mu\text{m}$.

2. Principle

Electron motion in conventional electronic devices was handled statistically as particles. However, the wave property in electrons become dominant once characteristic dimensions reach below $0.1 \mu\text{m}$ and energy levels become discrete.

Devices that operate on such quantum mechanics phenomenon are usually termed quantum effect devices. The principle is based on the "superlattice" concept proposed in 1970 by Professor Ezaki of IBM. Superlattice is, as shown in Figure 2, made up of alternate layers of crystals that are as thick as the electron wavelength ($\sim 10 \text{ nm}$). Electron movement perpendicular to the membrane is restricted by the quantum well structure and as the quantization phenomenon intensifies, ultrahigh frequency Bloch vibrations appear. Ten years of the superlattice project that began in 1981 has produced basic technologies in many fields like the realization of the world's first logic computation basic integrated circuit¹ in the form of a resonant hot electron transistor (RHET) device that uses resonant tunnel effect. This has opened up new applications for quantum effect devices.

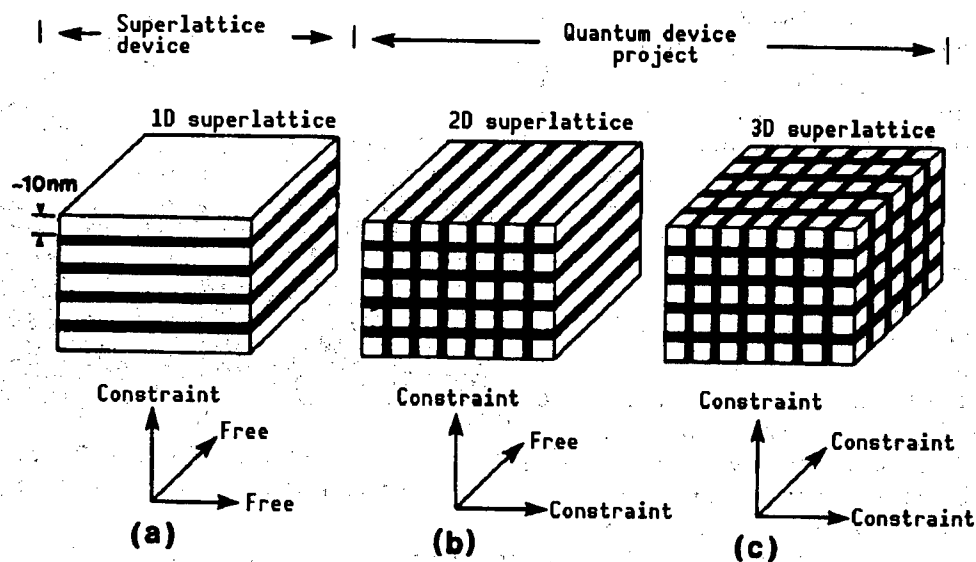


Figure 2. One-Dimensional, Two-Dimensional, and Three-Dimensional Superlattice Structure Concept of Electron Confinement Status

When quantum wire structures shown in Figure 2(b) become available, internal electron dispersion can be significantly reduced. As a result, electrons inside the quantum wire structures become highly mobile.² Coherent electron waves flow inside the thin and narrow leads and this led to the prediction of

various quantum effects due to the wave property in electrons. As shown in Figure 2(c), a quantum box structure will further split the discrete electron energy levels inside the quantum well. Quantum effects like suppression of electron dispersion mechanism, various interquantum level transitions between neighboring quantum wells and highly effective carrier insertion becomes a reality.

3. R&D Scope and Principle of Devices

The quantum functional device project is characterized by its emphasis on the development of a completely new integration system by applying quantum effects to devices. The devices targeted for development in this project thus must satisfy the following conditions:

Operational at temperatures near room temperature: Devices that only operate at helium temperature will be difficult to realize. Operation of devices should be verified at above 77 K.

Integratable: Integration is difficult when separation of I/O signals or amplification is insufficient even when each individual device operates perfectly which would then limit application to sensors.

Quantum mechanics phenomena appear in many forms but the devices that can be developed are limited by the aforementioned conditions. The devices developed are classified into three groups whose principles are described below.

(1) Quantum microstructure device

Electron tunnel effect, nondispersive ballistic effect, and single electron tunnel effect are employed in the ultrafine structure of this device. The basic principle of the tunnel control device is shown in Figure 3. As shown in the diagram, electrons can tunnel across the wall obstacle in the form of an insulative layer as thin as the electron wavelength inside the semiconductor. This effect appears in the derivative negative resistance in V-I characteristics which are well known in the Esaki diode. The tunnel effect itself is very fast and since it does not depend on temperature, its application to high-speed devices that operate at room temperature is attracting attention. However, circuit design is limited in two terminal devices

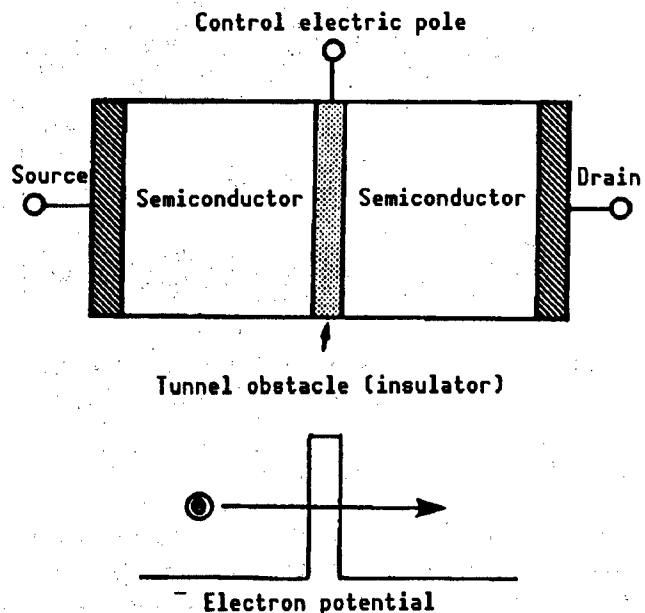


Figure 3. Basic Concept Diagram for Tunneling Control Device

and integration is also difficult. If, as shown in Figure 3, a third electrode can be attached to the tunnel wall obstacle for fabricating a three-terminal device modified by the thickness or the height of the obstacle, then the above disadvantages can be overcome.

(2) Quantum level device

This is a device that operates on inter electron energy level transition in a quantum well. Fabrication of a quantum well structure with several 10 nm insulator as the semiconductor active layer shown in Figure 4(a) will quantify electron energy levels as shown in Figure 4(b) such that a fixed number of electrons can be stored. Application to large memory capacity devices is promising. An electric field across the quantum well allows electron transition between the energy levels that constitute the quantum well thereby making logic devices feasible.

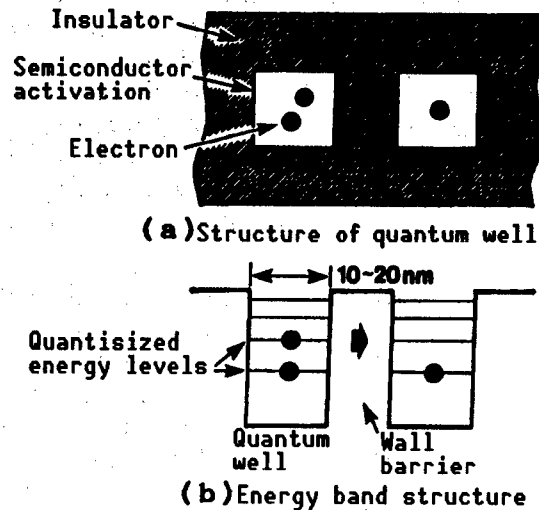


Figure 4. Structure of Quantum Well and Concept of Energy Band Structure

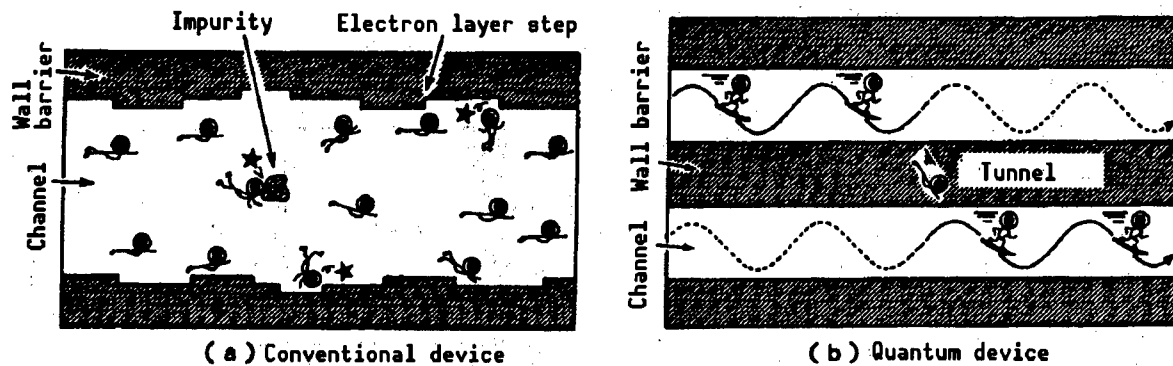


Figure 5. Comparison Between Electron Flow in Channels of Conventional Devices and Quantum Size Thin Devices

(3) Quantum wave device

This uses the electron wave property within the semiconductor and its operation principle is based on quantum wave phenomena like interference, reflection, and diffraction. As shown in Figure 5(a), electrons in conventional semiconductors collide with impurities, atomic layer step or lattice and as a result, the speed of the electrons becomes saturated and can no longer be increased even if an accelerating electrical voltage is applied. Therefore, the interference effect in electron wave meeting such frequent collisions will

not be apparent. However, electron dispersion is suppressed when a quantum thin lead is used. As a result, electrons will be extremely mobile and the phase of the electron wave will be preserved. Electron waves can be made to transition between one channel in a lead to another by the resonant tunnel effect when several such leads are placed next to each other. Realization of ultrahigh-speed and low power consumption is expected.

4. Factor Technologies and Targets in R&D

4.1 Factor Technologies

The following technique breakthroughs must be achieved before the aforementioned devices can be realized.

(1) Fabrication and evaluation techniques for quantum structures

Methods to fabricate minute structures that incorporate quantum functions and ways to evaluate the devices fabricated.

(2) Control techniques for quantum functions

Methods to effectively control quantum functions by measuring and analyzing the various physical phenomena in quantum structures.

(3) Factor device fabrication techniques using quantum functions

Fabrication and evaluation techniques for factor devices required to create unit functions in integrated systems by taking advantage of quantum functions.

(4) Integrated systems fabrication techniques

Methods to fabricate integrated systems exhibiting the required high-level information processing functions by organically bonding many factor devices.

4.2 R&D Target and Method

Phase One (FY 1991~1994)

Study and evaluate quantum functions and at the same time, develop device fabrication techniques once the device image is identified.

Phase Two (FY 1995~1997)

Based on results from Phase One, develop basic technologies and investigate methods to trial produce, evaluate, and integrate factor devices based on quantum functions.

Phase Three (FY 1997~1999)

Improve basic technologies for quantum functional devices to an advanced level and develop basic technologies to fabricate advanced factor devices and integrated systems.

Research and development will be performed in a parallel fashion and research status and results for each of the above phases will be evaluated whereupon a decision will be made to either stop or to continue with development. Domestic and international trends and funding will be monitored for smooth development.

5. Results To Be Expected

This basic and advanced research project produces unexpected results while forecast results sometimes cannot be obtained. Although the influences of this project cannot be predicted, applications may, at this stage, be those shown in Figure 6.

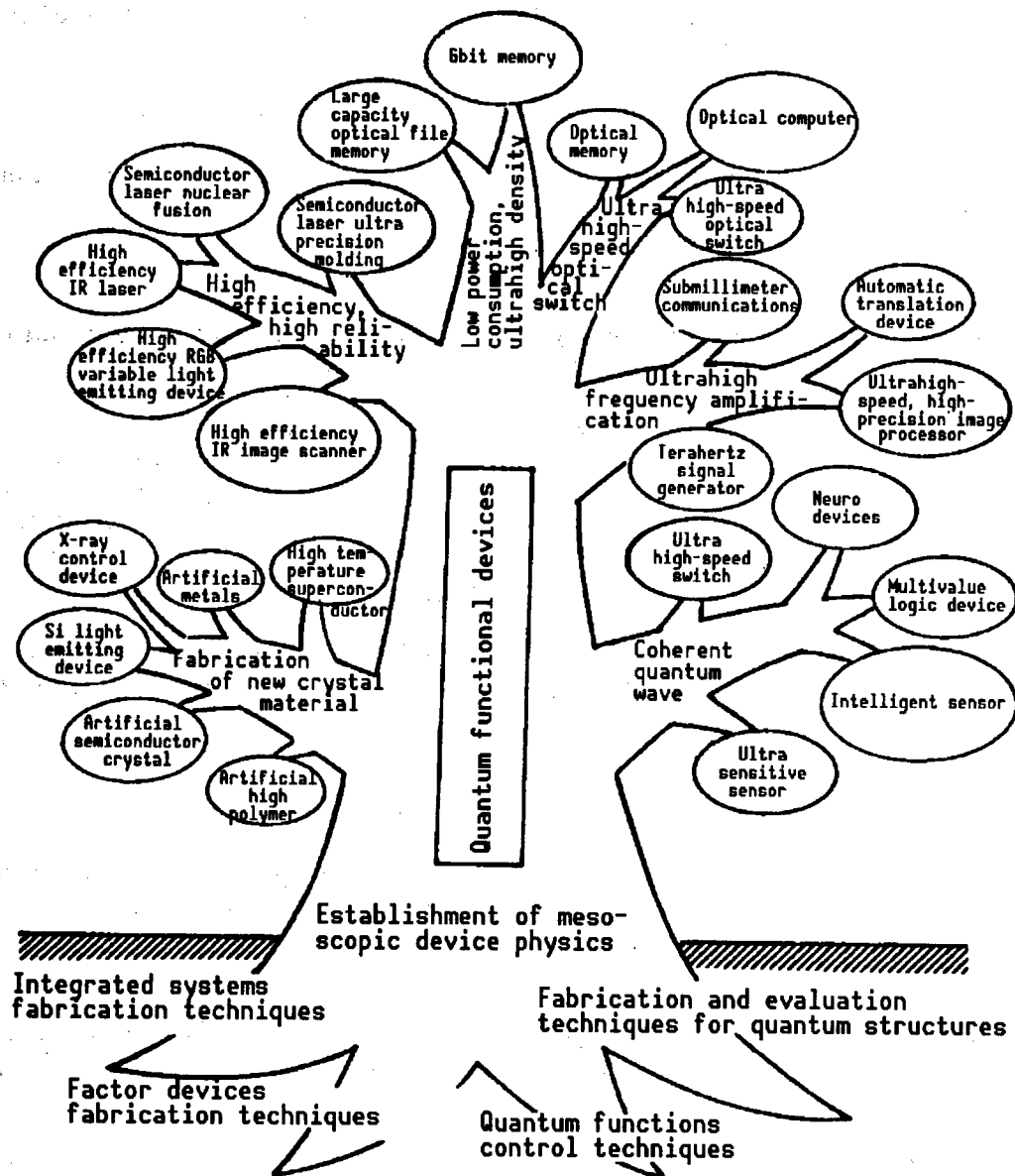


Figure 6. Influence of R&D on Quantum Functional Devices

6. Conclusion

Quantum effects were until recently only something that we read about in physics textbooks but with the domestic and international basic physical research in the mesoscopic domain, quantum phenomena can now be relatively easily handled in the light absorption. The world's interest is also on the increase. However, research and development to realize integrated devices whose quantum phenomena are technically controlled do not exist at all. The results of this project will be mankind's "common heritage."

References

1. Imamura, K., et al., Proceedings of Cornell Conference, 1991.
2. Sakaki, H., JPN. J. APPL. PHYS., Vol 19, 1980, p L735.

Overview on 'Model for New Software Structure' Project

926C0071W Tokyo SEKAI NI HABATAKU JISEDAI PUROJEKUTO in Japanese 19 Feb 92
pp 167-168

[Article by Yuichiro Tamura, Electrotechnical Laboratory]

[Text] 1. Purpose

The "Model for New Software Structure" project was the first information processing related project in the Jisedai Project. It was launched in 1990 and its purpose is "the development of a new software structure model that allows improvement of software used in production, significant expansion of the scope of their reapplication as well as the creation of user friendly software. The basics for the software industry in the next generation can be established through research which must be approached from several standpoints like common computer or system structure. Another target is the establishment of basic configuration and the theory behind software that respond to changes in the environment."

2. Details

The target in this project is the "revolutionization" of software architecture. The research theme of the structural model should thus be changed to architecture which means "ways to connect, bond, or join parts together." This project was launched with the assumption that issues recognized prior to its launching cannot be resolved unless we revolutionize our way of thinking.

This was a result of criticism and reconsideration of our software engineering stigma that forces us to write specifications in natural language or to write software in detail. In fact, the configuration of software required by most users cannot usually cope with that which is evident from recent high-level personal computer software.

Is software sufficiently easy to use and create?

3. Current Software Technology and Related Issues

Software technology trends seem to indicate a general popularization in the 1990s of the object-oriented paradigm that ruled the past 20 years as a result

of its ease of creation and use when compared with others. Is this satisfactory? Interpretation of issues and their resulting measures will depend on the interpretation of the object-oriented paradigm. Let us assume the standard interpretation. The disadvantage of this paradigm is its lack of strong mutual interaction with the ambient environment. I do not mean to say that it does not have any interaction. But, interpretation of the messages received, execution depending on that interpretation and then self-reconfiguration (by producing images) are extremely simple and lack intelligent functions like interpretation in response to conditions, autonomous behavior as a result of self-will, adjustment to environmental changes, and finally "learning."

There is some software that partially performs these functions. For example, environment adjusting software is commonly used in network bridges. But this has not been thoroughly studied, standardized or even systematized.

The target in this project is the incorporation of such intelligent functions (mutual interaction with the environment is one basic intelligent function) into the object. What then should be the mechanism for realizing this objective? What should the basic theory be? What are the issues and what kind of measures should be taken? These are some of the questions that remain. The eight years research may, in fact, be too short. I believe that the results of this project will only reach the general public about 10 years after its completion. This is the time it will take for techniques to be polished and the general public to understand the principles as is proved by the object-oriented paradigm.

4. Project Participants

One characteristic of this project is the diverse background of its participant researchers. This project is made up of four sectors.

- (1) National research institutes: Electrotechnical Laboratory and Mechanical Engineering Laboratory
- (2) 13 private corporations
- (3) Domestic academic sector that includes Tokyo Institute of Technology, Keio University, Tokyo University
- (4) Foreign research team that included SRI, Stanford University, Oxford University

Each sector is in charge of a different theme but all have the same final goal—a characteristic that is not commonly seen in conventional MITI projects.

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